DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
George K. Burgess, Director

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PHYSICAL PROPERTIES OF DENTAL MATERIALS (GOLD ALLOYS AND ACCESSORY MATERIALS)

By R. L. Coleman

ABSTRACT

The physical properties of dental gold alloys used in the wrought and cast states, investments, and pattern waxes were investigated. Practicable methods of testing these materials were developed, and these methods and the apparatus used are described. The properties of a large number of representative commercial materials were determined and the values reported. Especial attention was given to those properties having a direct bearing on the usefulness of these materials in the construction of mechanical dental appliances and to the effects of variations in manipulative procedures. Improvements in methods of manipulation, especially in the dental-casting processes and in the heat treatment of gold alloys, were developed. It was found that the dental gold alloys on the market vary widely in their mechanical properties and fusion temperatures as well as in chemical composition. This emphasizes the necessity for selecting suitable materials for specific purposes on the basis of tests of physical properties. The methods of testing developed and described herein provide the dental profession and schools with a means of grading and selecting materials on this basis.

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I. INTRODUCTION

In 1919 the National Bureau of Standards was asked to assist one of the Government departments in grading or selecting satisfactory amalgam alloys for its use and in establishing specifications upun which such alloys could be purchased. This was done, and the results [1] were published in 1920.

These reports were favorably received, and numerous requests were made by individuals and organizations that the work be extended to include the problems met in the use of gold alloys. Owing to a lack of sufficient funds the bureau was unable to assume full responsibility for such an elaborate program as appeared necessary. The research associate plan [2] in operation at the bureau, by which outside organizations may cooperate in financing and carrying on research of especial interest to them, was available to the dental societies or associations, but only one of the interested organizations, the Weinstein Research Laboratories, of New York, N. Y., offered to provide the necessary cooperation. This offer was accepted and the work started in January, 1922.

The conditions under which this work was carried on were briefly as follows:

1. The cooperating laboratory paid the salaries of the associates, provided all special equipment, and supplied funds for purchasing materials to be tested.

2. The bureau provided the facilities of its laboratories and the cooperation and advice of its scientific staff, supervised the work, and published the results.

A tentative outline of the program of research [3] was published in the Journal of the American Dental Association with a request for criticisms and suggestions from interested members of the profession. A number of valuable suggestions were received, and these were incorporated into the final program. This program included studies of the important properties of dental gold alloys in the wrought and cast forms, pattern waxes, investments, impression and cast materials, and the effects on these materials of variations in manipulative procedure. The purposes of these studies were: (1) To establish methods of testing these materials; (2) to determine the important properties of a number of representative products; and (3) to develop such improvements in the methods of manipulating these materials as might be suggested by a better understanding of their properties.

[1] Souder, W. H., and Peters, C. G., An Investigation of the Physical Properties of Dental Materials, B. S. Tech. Paper No. 157; 1920; Dental Cosmos, **62**, p. 305; March, 1920.

[2] For a description of this plan see Bureau of Standards Circular No. 296, Research Associates at the Bureau of Standards.

[3] "Dental research"; J. A. D. A.; March, 1924.

A number of progress reports [4] on various phases of the work were published in the dental journals from time to time as data were obtained. The present paper consists of a collection and correlation of the data previously reported with such additional data as are now available.

The author wishes to make the following acknowledgments, in addition to those made in the text:

1. The cooperative research by the Bureau of Standards and the Weinstein Research Laboratories reported in this paper was planned jointly by Louis J. Weinstein, director of the Weinstein Research Laboratories, and Wilmer Souder, physicist, of the Bureau of Standards, who is actively in charge of this work. Their continued aid throughout has been essential to its success. Doctor Weinstein, by reason of his pioneer work and long experience in this field, has been able to contribute valuable aid on the dental problems involved. Doctor Souder directed the scientific phases of the research. Acknowledgment is also made of their assistance in interpreting the results and preparing the material for publication.

2. W. A. Poppe, research assistant, Bureau of Standards, assisted in this work.

II. GOLD ALLOYS

In the investigation of the physical properties of dental gold alloys those properties having a direct bearing on the usefulness of the alloys as materials of dental construction were given major consideration. Among the more important of these are the various mechanical properties, such as strength, hardness, ductility, and others. An extensive investigation was undertaken to determine these properties and the manner in which they are affected by various heat treatments and manipulative procedures. Other important properties studied are chemical composition, melting range or fusion temperature, and, in the case of alloys used in the cast state, casting shrinkage. Microscopic examinations were made chiefly to help explain variations in the mechanical properties and to supplement chemical analysis as an identification of the material.

In determining the mechanical properties of these alloys it is essential that the test specimens be of such size and produced under such conditions as to be representative of the materials as actually used for dental purposes. Thus, tests of an alloy intended for use as

[4] (*a*) Souder, Wilmer, "Physical properties of dental materials"; J. A. D. A.; May, 1925. (*b*) Coleman R. L., "Physical properties of dental materials II (wrought gold alloys)"; J. A. D. A.; May, 1925. (*c*) Coleman. R. L., "Physical properties of dental materials III (progress report of research on the dental casting, process)"; Dental Cosmos, August, 1926. (*d*) Swanger, William H., Analysis of Dental Gold Alloys, B. S. Sci. Paper No. 532; J. Dental Research, December, 1927. (*e*) Souder, Wilmer, "The selection of dental materials"; J. A. D. A.; February, 1927. (*f*) Coleman, R. L., "Physical properties of dental materials IV (cast gold alloys)"; Dental Cosmos, October, 1927. (*g*) Souder, Wilmer, "Summary of reports on dental alloys"; J. A. D. A.; April, 1928.

clasp or orthodontia wire would not be conclusive if test specimens of the size commonly recommended for structural steel were employed. Nor would the results of tests of an alloy in the wrought condition be a reliable index of the usefulness of that alloy when employed in the cast state.

In selecting apparatus and methods of test these considerations were kept in mind. In a number of instances it was necessary to modify the usual methods or to develop special apparatus adapted to the peculiar characteristics of the materials being tested. It was found that much of the equipment suitable for testing small wires, plate, and band material was unsatisfactory when applied to cast specimens. For this reason it was deemed advisable, for the purposes of this investigation, to divide the dental gold alloys into two groups according to the form in which they are used; namely, wrought alloys and cast alloys. This grouping will be adhered to in the following discussion of these materials.

The alloys tested were selected from those on the market and are believed to be representative of the better grade of materials available for the construction of mechanical dental appliances. The selections were made chiefly on the basis of the manufacturers' claims of superiority for specific uses. Except where otherwise stated, the samples were purchased in the open market and were received in original packages.

Eighteen wrought alloys were selected as being representative of the materials available for use in this form. Included in this list are alloys recommended by their respective manufacturers for use as wire or flat clasps, orthodontia arch and spring wires, and plate and bands of varying properties intended for a number of different uses. Eight of these alloys were tested in the form of round wire and 10 in the form of flat strip.

The group of cast alloys tested consists of 35 alloys selected as being representative of each of the general types of casting golds in use. Included in this list are a number of the so-called hard alloys intended for clasps, bars, and similar uses, and others of the types intended for such uses as hard inlays or three-quarter crowns, partial dentures, full dentures, and soft inlays. Gold solders of three grades commonly employed in dental practice are also included.

It should be pointed out that most of the alloys tested were purchased during or prior to 1925. Since that time some of these alloys have been modified or discontinued, and new alloys have been put on the market. However, it is believed that the list selected is still representative of the materials available.

In accordance with a general policy of the bureau the trade names of these alloys are not given. Instead each alloy is designated by a letter or number. The designations are entirely arbitrary and have

no reference to the trade names or to the relative merits of the alloys. If the trade names are desired, they may be obtained from the manufacturers who will recognize their product from the chemical analysis.

Descriptions of the methods of testing used as well as the values obtained will be presented in the following sections. No attempt will be made to give all details of the usual routine methods and requirements for accurate testing. These may be had by reference to any standard text [5] of the testing laboratory or engineering school.

1. WROUGHT ALLOYS

(a) CHEMICAL COMPOSITION

Chemical analyses of all the wrought alloys tested were made for purposes of identification and in order to correlate variations in physical properties with corresponding variations in chemical composition. The analyses were made by William H. Swanger, research associate. For the purposes of this investigation it was desirable that the compositions be determined with the highest possible accuracy. For this reason it was necessary to modify many of the analytical methods previously used and in some instances to develop new methods. A description of the methods used is given in a previous publication,[6] reference to which should be made for the detailed procedure. In order to indicate the accuracy attained, it may be stated that in most instances the agreement between duplicate determinations of the major constituents was better than 0.1 per cent (calculated on the sample) with a proportional precision for minor constituents. All analyses were made in duplicate, and the average values reported.

The compositions are given in Table 1. A study of these values reveals that alloys of this group are composed chiefly of gold, silver, copper, and platinum or palladium. In most instances small amounts of one or more other metals, such as zinc, tin, nickel, manganese, iron, magnesium, iridium, and rhodium, are present. Some of these are added intentionally to alter the properties of the alloy, while others are undoubtedly present as impurities in the major constituents. As many as nine of the above-named metals were found in a single alloy.

The proportionate amounts of the major constituents were found to vary widely even in alloys intended for the same or similar uses. A striking example of this is found in the group of alloys supplied in wire form; namely, alloys A to H, inclusive. These were intended for use as clasps or orthodontia arch or spring wires, the requirements for which, from a consideration of the mechanics involved, are very

[5] The following are examples of such textbooks. Mechanical Testing. Two volumes. Batson and Hyde, E. P. Dutton & Co., New York; 1923. Handbuch des Material Prüfungswesens, Otto Wawziniok, Julius Speringer, Berlin, Germany; 1923.

[6] See footnote 4 (*d*), p. 869.

similar. The wide variations in the compositions of these alloys are obvious from an inspection of Table 1. It will be noted that the total gold, platinum, and palladium content of the alloys of this group, alloys A to H, inclusive, varies, in general, from about 75 to about 85 per cent. There are, however, two notable exceptions; namely, alloys B and G. In the case of alloy B the total of these three metals is only about 50 per cent, while in the case of alloy G it is about 99 per cent.

TABLE 1.—*Chemical composition of wrought alloys (per cent by weight)*

Alloy	Silver	Gold	Platinum	Palladium	Copper	Zinc	Nickel	Iridium
A [1]	5.1	64.5	17.6	2.1	10.4	0.8		
B [2]	36.4	41.7	.1	8.3	9.4	.3		
C	7.7	59.3	18.3	1.6	13.0			0.2
D	15.2	62.6	10.4	.2	11.8			
E	15.0	59.5	15.2		8.8		1.3	
F	15.4	60.9	16.0	.2	6.7	.3		.5
G	.2	66.2	13.3	19.4	.2	.1		.5
H	9.9	61.9	16.0		12.1	.1		
I [3]	11.0	60.0	13.1	5.9	8.9	.72		.2
J	17.7	62.9	12.3		6.7	.1	.08	
K	5.0	63.9	13.5	10.2	7.1	.2		.15
L		75.6	7.0	16.1		.07		1.2
M [4]	9.3	62.3	22.8	.5	4.5	.1	.02	.4
N	7.3	81.2	7.0		4.3	.1		
O	.04	89.8	.08		10.0			
P		67.3	1.0	31.8				
Q	.01	89.8	10.0		.07	.02		
R	.1	90.6	9.3			.02	.01	

[1] Tin 0.16 per cent.
[2] Manganese 3.8 per cent; magnesium 0.1 per cent.
[3] Tin 0.14 per cent.
[4] Iron 0.2 per cent.

The complexity of the compositions of these alloys and the apparent lack of systematic ratios for the elements present indicate that their formulas are largely empiric.

The effects of some of the variations in composition on the physical properties of these alloys will be discussed as the various properties are reached.

(b) MICROSTRUCTURE

In view of the questionable manner in which this subject has been treated in some of the dental literature it is deemed advisable to preface this section with a brief statement of some of the practical applications and limitations of the study of microstructure as applied to the complex gold alloys. This should serve to obviate the possibility of misinterpretation of the micrographic data presented in this paper.

The suitability of an alloy for any mechanical use whatever, not alone its applications in dentistry, should be judged principally by its mechanical properties. The study of microstructure, when correlated with data on chemical composition and other characteristics, is

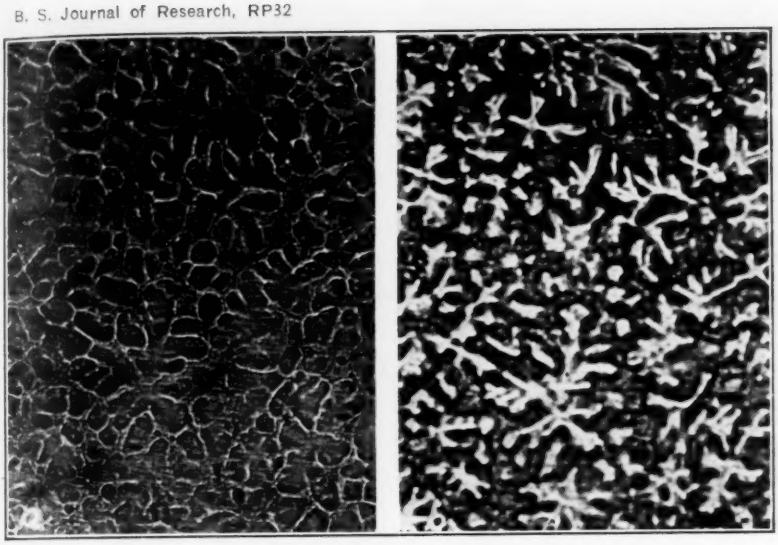

FIG. 1.—*Deceptive micrographs of a cast gold alloy*

a and *b* are identical except for change in focus, × 90

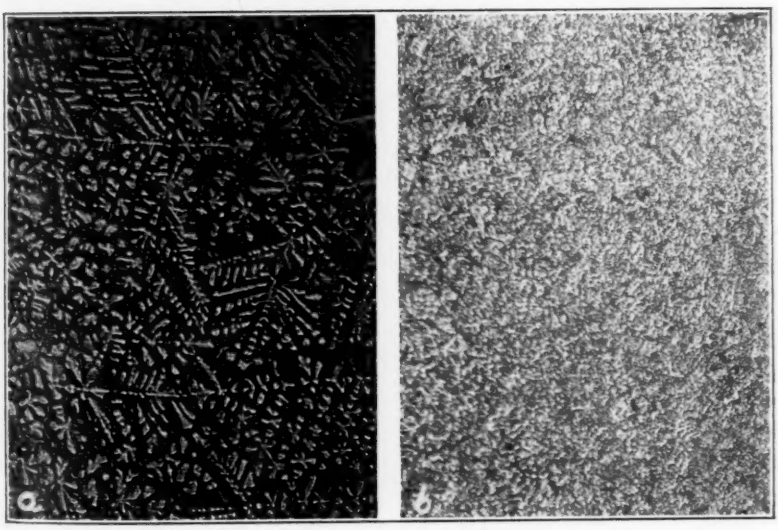

FIG. 2.—*Microstructure of alloy A*

a Cast and slowly cooled, × 50. The dendritic structure is characteristic of solid solutions.
b, Cross-sectional structure of a wire of alloy A hardened, × 450.

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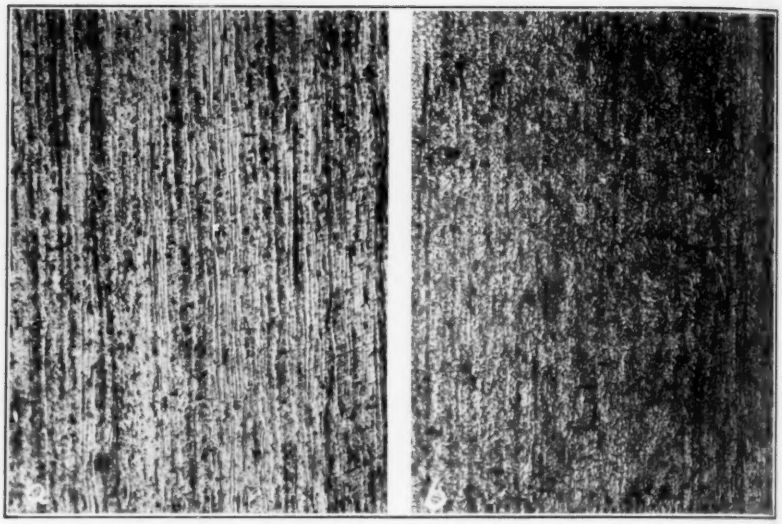

FIG. 3.—*Microstructure of alloy A; longitudinal sections of wire,* × 450

The dendrites of the solid solution shown in Figure 2(*a*) have been elongated and ruptured in the drawing process and now appear as light portions elongated in the direction of drawing. *a*, Softened; *b*, Hardened.

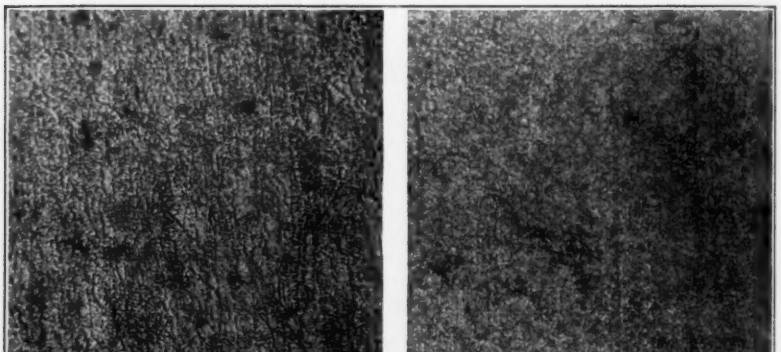

FIG. 4.—*Microstructure of alloy A; longitudinal section,* × *450*

Heat treatments; *a*, Softening followed by hardening; *b*, Softening, followed by hardening and a second softening. These structures appear to be quite similar, but the mechanical properties are very different.

of value, but the final criterion must be the mechanical properties or the behavior of the material under service conditions.

In undertaking the study of microstructure of these alloys it was hoped to attain the following objects:

1. To supplement chemical analyses as an identification of the materials tested. It is well known that the properties of an alloy are affected by mechanical and heat treatments. Thus, the mechanical properties of a cast rod would not be expected to be the same as those of a wrought rod of identical composition, nor would the properties of the wrought rod be identical with those of the same rod after being subjected to certain heat treatments. The micrograph should help to define the condition of the alloy with respect to these factors.

2. To reveal microscopic defects, if present, due to casting or mechanical working.

3. To determine the homogeneity of the alloys and the presence of certain impurities.

4. To obtain some information concerning the constitution of the alloys that might help explain how and why their properties may be changed by heat treatment.

It should be borne in mind that while the microscope may reveal the existence of certain conditions it does not determine the effects of these conditions on the mechanical properties of these complex alloys. This can be done only by determining the mechanical properties themselves.

In obtaining micrographs truly representative of the specimens under test the preparation of the alloy surface, the etching, the method of illuminating, the focusing and various other factors are of great importance. Accidental or intentional errors in any one of the steps are sure to vitiate the result. Figures 1 (*a*) and (*b*) are included to illustrate this. The two micrographs are from the identical surface and position. The marked difference in the appearance of the structure is due entirely to a slight change in focus.

From the foregoing it is evident that the value of a study of microstructures is very limited unless this study is correlated with that of the other important characteristics of the material and that micrographs presented without sufficient data would be meaningless. The following micrographs are presented with the foregoing conditions fully in mind.

There appeared to be some lack of uniformity of materials as received, perhaps owing to differences in mechanical working or heat treating at the factory. It was found that this could be largely eliminated and in many instances the alloy made either hard or soft at will by proper heat treatment. The methods of heat treating and the corresponding effects on the mechanical properties are described in detail in following sections of this paper. Briefly, the heat treat-

ments employed were as follows: For softening the alloy was heated to 700° C. (1,290° F.) and quenched in water; for hardening the alloy was heated to 450° C. (840° F.) and cooled slowly.

The microstructure of the material as received was considered of little interest since it is usually advantageous to soften the alloy before shaping it into the desired form and later to harden the finished appliance. For this reason micrographs were made of the alloys after heat treating as indicated above. All the samples reported in this section were etched with aqua regia.

Figure 2 (*a*) shows the structure of alloy A when cast and cooled slowly. The dendritic structure shown is characteristic of solid solutions. This structure does not preclude the presence of intermetallic compounds which may be present, but not shown by the microscope.

Figure 2 (*b*) shows the cross-section structure of a wire of alloy A 0.035 inch in diameter, and Figures 3 and 4 show longitudinal sections of the same wire. The parallel lighter grain structure shown in Figure 3 (*a*) and some of the following micrographs is the dendrite elongated and distorted in the drawing, rolling, or swaging process. Such structures have been referred to in some of the dental literature as indicating segregation of some of the constituents. While it may be possible to call these lines segregations in a very special sense, they are not segregated in the sense of defects due to melting, casting, or working, but are normal characteristic structure for this type of alloy when subjected to this treatment.

The specimen shown in Figure 3 (*a*) was given the softening heat treatment, and that shown in Figure 3 (*b*) was given the same treatment followed by the hardening heat treatment. In the case of the latter specimen the severely worked structure has been changed to the more nearly homogeneous structure of an annealed alloy. This structure appears to be permanent as giving the specimen a second hardening heat treatment, as shown in Figure 4 (*a*), or a second softening treatment, as shown in Figure 4 (*b*), did not appreciably modify the microstructure, although, as will be shown later, such treatment does change the mechanical properties.

Figure 5 shows the structure of alloy B. Figure 5 (*a*) shows the structure of the alloy quenched in water from 700° C. (1,290° F.) and Figure 5 (*b*) that of the alloy quenched, reheated to 700° C. (1,290° F.), and then air cooled. These treatments correspond to the recommendations of the manufacturer so far as we are able to interpret them.

The heat treatments given the alloys shown in the remaining sets of micrographs, Figures 6 to 11, were the softening treatment, shown at (*a*), and the softening treatment followed by the hardening treatment, shown at (*b*). All of these micrographs were made at a magnification of 450.

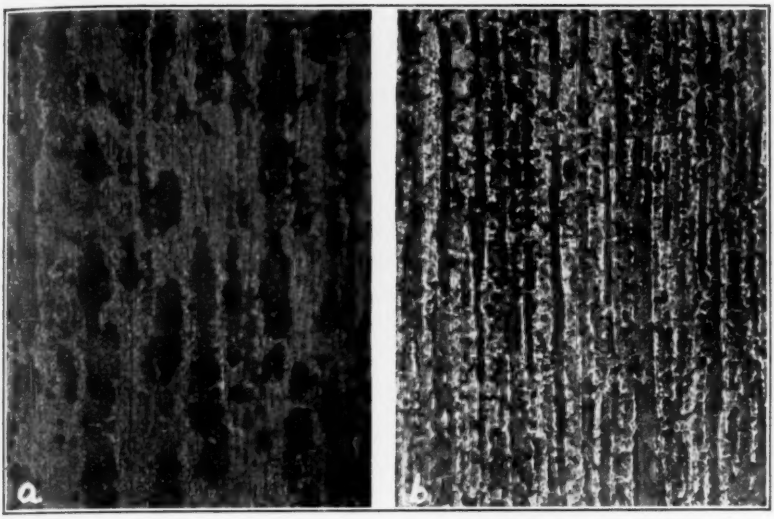

FIG. 5.—*Microstructure of alloy B; longitudinal section, × 450*

a, Softened; *b*, Cooled in air from 700° C.

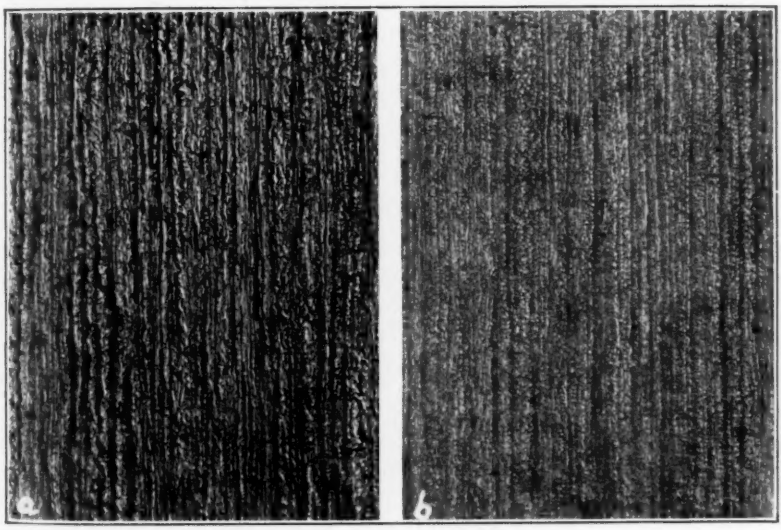

FIG. 6.—*Microstructure of alloy C; longitudinal section, × 450*

a, Softened; *b*, Hardened

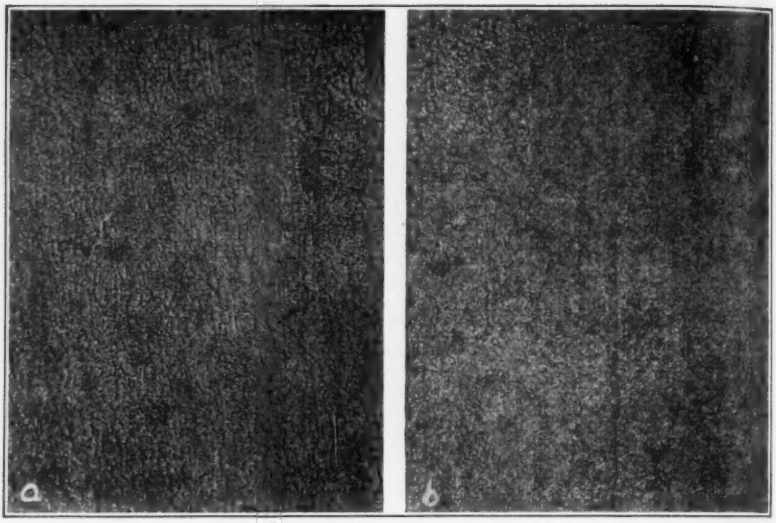

FIG. 7.—*Microstructure of alloy D; longitudinal section,* × *450*

a, Softened; *b*, Hardened

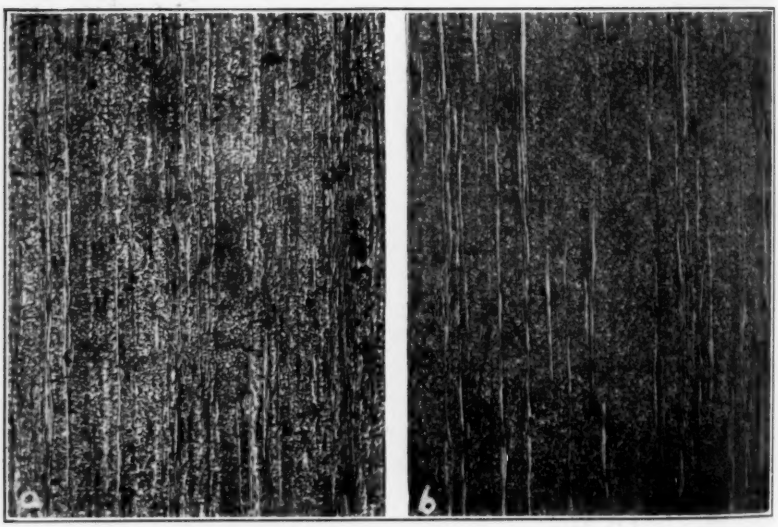

FIG. 8.—*Microstructure of alloy E; longitudinal section,* × *450*

a, Softened; *b*, Hardened

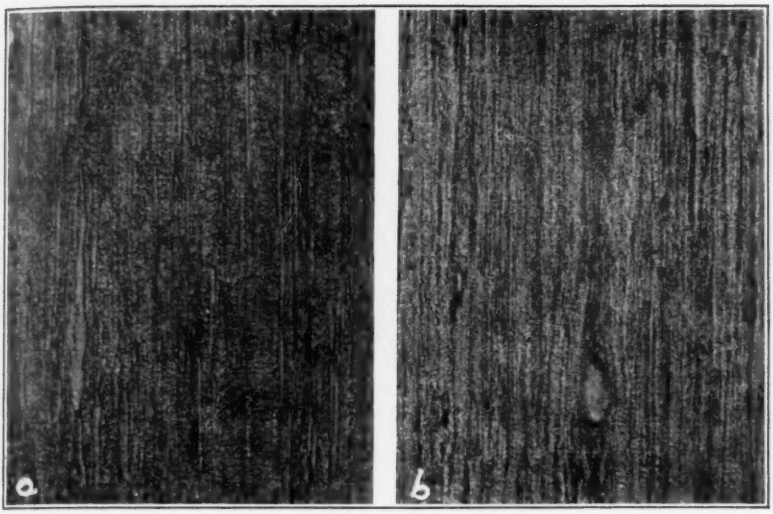

FIG. 9.—*Microstructure of alloy F; longitudinal section,* × *450*

a, Softened; *b*, Hardened

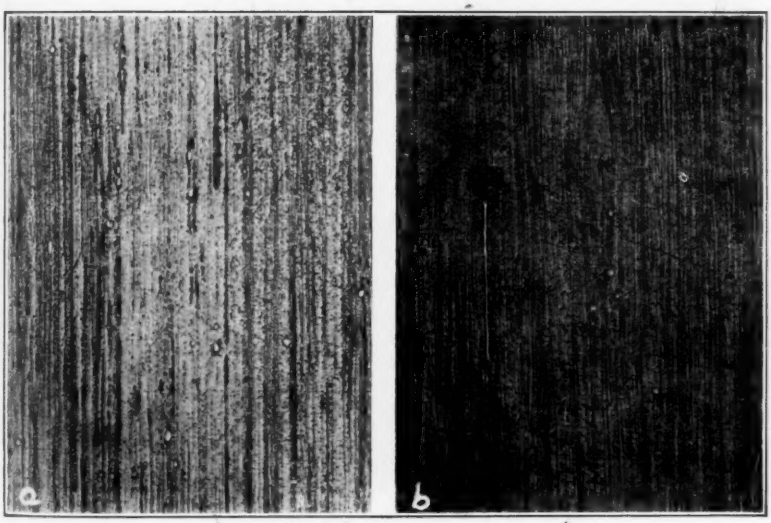

FIG. 10.—*Microstructure of alloy G; longitudinal section,* × *450*

a, Softened; *b*, Hardened

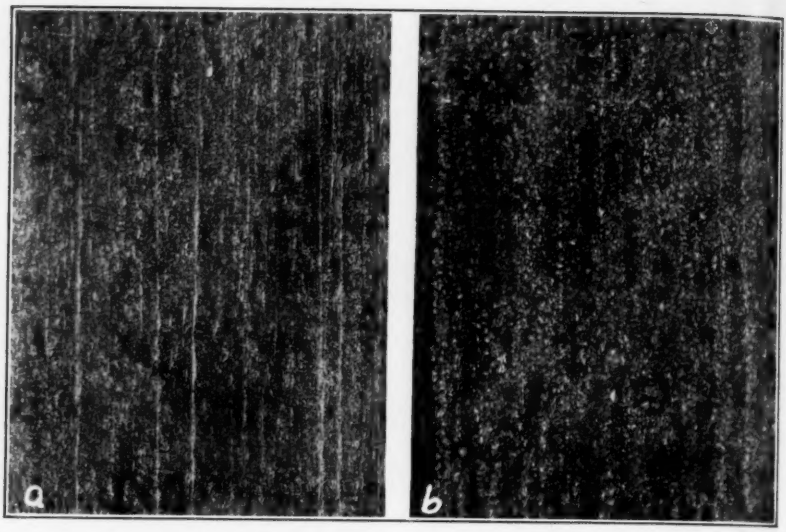

FIG. 11.—*Microstructure of alloy H; longitudinal section,* × *450*

a, Softened; *b*, Hardened

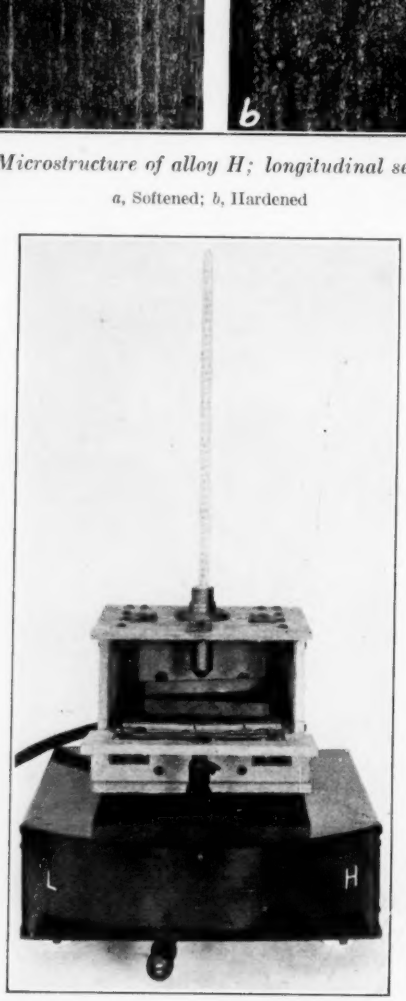

FIG. 14.—*Box-type electric furnace used for heat treating short wires*

The micrographs of alloy D in the softened and hardened conditions, shown in Figure 7, are very similar and do not show the typical worked structure. It is concluded that the heating to 700° C. (1,290° F.) incident to the softening treatment is sufficient to change the worked structure of this alloy, or that this wire was heat treated before leaving the factory. This pair of micrographs is not unlike those of Figure 4.

In many cases the softened specimens still retained some evidences of severe working in drawing or swaging. To some extent this structure was modified by the later and more prolonged hardening heat treatment. The prominent lines representing the elongated dendrites of the worked alloy became less distinct, probably due to diffusion, resulting in a more nearly homogeneous structure. In some instances there were indications of incipient grain growth or recrystalization. This is more noticeable in Figures 4 (*a*), 7 (*a*), 7 (*b*), and 11 (*b*). Evidences of serious defects due to casting or working, oxide or other inclusions, or to segregations were not found.

It was noted that in the case of those alloys capable of being appreciably hardened by heat treatment the specimens in the hardened condition were more resistant to etching than those in the softened condition. This indicates that these alloys may have their resistance to the actions of mouth fluids increased by the hardening heat treatment. As will be shown later this treatment will greatly improve their mechanical properties.

(c) FUSION TEMPERATURES

Complex alloys seldom have a single, definite melting temperature such as the pure metals have, but usually have a definite melting range or temperature interval within which part of the alloy is in the liquid and part in the solid state. The alloy begins to melt at the temperature of the lower limit of the range but is not completely melted until the temperature of the upper limit is reached. Table 2, giving the melting points of some of the metals used in dental alloys and the melting ranges of a binary alloy of each of these metals with gold, is included to illustrate this and for reference purposes. It will be noted that the length of the melting range of an alloy varies widely, depending upon the metals of which it is composed. The range for an alloy containing 90 per cent gold and 10 per cent silver is only 6° C., while that of an alloy containing 90 per cent gold and 10 per cent platinum is nearly 130° C. Some of the complex alloys used in dentistry have melting ranges even longer than this. Such temperature ranges are usually determined by observing changes in the time rate of cooling of the alloy as it passes from the liquid to the solid state. Two determinations of this kind are illustrated in Figure 12.

TABLE 2.—*Melting points and ranges of a few elements used in dentistry and some of their binary alloys*

Element or alloy	Melting point or range	
	Centigrade	Fahrenheit
Gold	1,063	1,945
Platinum	1,755	3,191
Palladium	1,549	2,820
Nickel	1,152	2,106
Copper	1,083	1,981
Silver	960	1,760
Zinc	419	786
90 per cent gold, 10 per cent zinc	679– 696	1,254–1,285
90 per cent gold, 10 per cent copper	926– 940	1,699–1,724
90 per cent gold, 10 per cent nickel	935– 966	1,715–1,771
90 per cent gold, 10 per cent silver	1,046–1,052	1,915–1,926
90 per cent gold, 10 per cent platinum	1,062–1,191	1,944–2,176
90 per cent gold, 10 per cent palladium	1,270–1,287	2,318–2,349

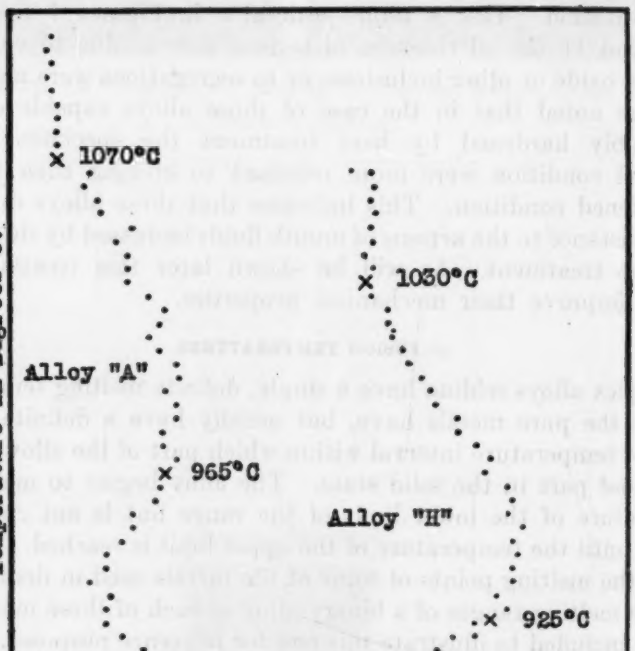

FIG. 12.—*Cooling curves for alloys A and H*

The time required for the alloy to cool equal temperature intervals is plotted against temperature. This is known as the inverse rate method and locates the freezing range. The temperature at which the molten alloy begins to freeze is indicated by a decrease in the rate of cooling: 1,070° C. for alloy A and 1,030° C. for alloy H. Solidification of the alloy is complete when the rate of cooling shows a sudden increase; 965° C. for alloy A and 925° C. for alloy H

In the case of a wrought alloy the upper limit of the melting range is of little practical importance to the user, since he seldom has occasion to completely melt the alloy. However, it is important to know the maximum temperature at which the alloy may be soldered, bent, or otherwise manipulated with safety. For the purpose of locating this temperature it was felt that sufficient data could be secured by determining a point within the melting range by means of the "wire" method.[7] A brief description of this method as employed in these tests follows. A short piece of the alloy (from 3 to 4 mm long), the fusion point of which was to be determined, was welded between the wires of a platinum and platinum-rhodium thermocouple to form the hot junction. After connecting this thermocouple to a potentiometer the hot junction was inserted in an electric furnace at a temperature somewhat below the fusion temperature of the alloy under test and the temperature raised at a uniform rate not exceeding 5° C. per minute. The temperature was indicated by the potentiometer. Care was taken to prevent a temperature gradient across the sample that might cause serious error in the indicated temperature. The fusion of the sample, causing a break in the connection between the wires of the thermocouple, was indicated by the potentiometer registering an open circuit.

Both limits of the melting range were determined for a few wrought alloys, and it was found that they were of no more value than the temperatures determined by the "wire" method and, perhaps, not so reliable in indicating the temperature at which failure could be expected. The "wire" method was, therefore, adopted. The fusion temperatures as determined by this method are given in Table 3.

TABLE 3.—*Fusion temperatures of alloys* [1]

Wire			Band or plate		
Alloy	Temperature [2]		Alloy	Temperature [2]	
	°C.	°F.		°C.	°F.
A	990	1,815	I	1,020	1,870
B	895	1,645	J	985	1,805
C	1,010	1,850	K	1,110	2,030
D	930	1,705	L	1,325	2,415
E	955	1,750	M	1,065	1,950
F	1,005	1,840	N	1,010	1,850
G	1,375	2,505	O	935	1,715
H	965	1,770	P	1,410	2,570
			Q	1,095	2,005
			R	1,100	2,010

[1] The author is indebted to H. M. Schmitt and W. F. Roeser for assistance in determining these fusion temperatures.
[2] Observations are to nearest 5°.

No comments are offered as to the most appropriate working temperature for such alloys. Certainly soldering, heat treating, or

[7] A detailed description of this method is given in B. S. Tech. Paper No. 170; 1921.

manipulating should not be attempted above the fusion temperature. For most purposes the temperature should be kept below this point. The nearness to which the fusion temperature may be approached with safety will depend upon the skill of the operator, the control of the furnace or flame, the quality of the solder used, and other factors. The temperature given may be taken as a maximum which should never be exceeded in any operation.

(d) HEAT TREATMENT

At the time this investigation was begun some data had been published on the subject of heat treatment of dental gold alloys, but it was found impossible to coordinate the findings of the different observers. The devices and methods for heat treatment recommended by most lecturers and clinicians were so general in their nature and lacked so much in detail that it was decided to make an independent investigation of this subject.

Preliminary experiments indicated that these alloys could be softened by heating to a temperature of about 700° to 800° C. (1,290° to 1,470° F.) and quenching in water, and that some, though not all of them, could be hardened by heating to the same temperature and cooling slowly. It was necessary to determine the proper temperatures and times or rates of cooling to produce these results efficiently under the practical working conditions of the dental laboratory.

Attempts to determine these constants by changes in cooling curves and thermal expansivity, induced by different heat treatments, were not conclusive. The most promising method appeared to be that of determining changes in thermal electromotive force. By making thermocouples of heat treated and untreated wires, and of wires subjected to different heat treatments, and observing the emf values for increasing temperatures, it was found that changes in thermoelectric properties were taking place within certain temperature ranges. Careful tests with wires prepared in the manner indicated by these first approximate findings served to narrow the range of temperature and time.

Figure 13 represents a typical curve obtained by this method. The values plotted in this figure were obtained from a thermocouple made of two alloy A wires. Both wires had previously been quenched in water from 700° C. (1,290° F.), and one was used in the quenched condition and the other after it had been reheated to 700° C. (1,290° F.) and cooled slowly. One end of the couple was placed in a furnace, the temperature raised at a rate of approximately 13° C. per minute, and the emf of the alloy A couple corresponding to various temperatures was recorded. It will be noted that the emf increases as the temperature is raised up to about 425° C. (800° F.) and then

remains approximately constant, indicating that a transformation has occurred and the portions of the two wires inside the furnace are now in the same condition. The indicated emf does not drop to zero, as might be expected after the furnace has reached the temperature at which the transformation is completed, because as the wires extend outside the furnace they pass through a temperature which is just below that at which the transformation is completed; hence, as the temperature inside the furnace is raised the indicated emf becomes approximately constant at the maximum value.

The temperature at which this transformation is completed, in this case approximately 425° C. (800° F.), was recognized as that at which the maximum change in the mechanical properties of the alloy was most likely to occur. Similar tests on this and other alloys using thermocouple elements that had been subjected to various heat treatments indicated that for these alloys the maximum

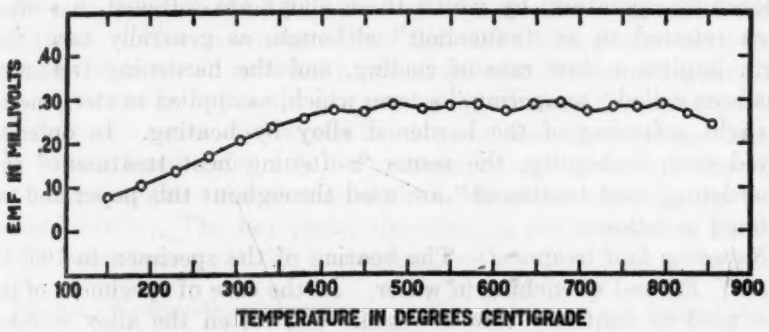

FIG. 13.—*Temperature emf relation for a thermocouple made of two wires of the same chemical composition but given different heat treatments*

softening effect could be secured by quenching from a temperature ranging from 700° to 800° C. (1,290° to 1,475° F.) and the maximum hardening effect by prolonged heating at a temperature ranging from 400° to 450° C. (750° to 840° F.) or by slow cooling from a temperature within or slightly above this range. These tests also indicated that varying degrees of hardening could be secured by prolonged heating at, or slow cooling from, temperatures both above and below the range specified and by varying the length of time the temperature was maintained or by varying the rate of cooling. It was also found that the time required to produce a given degree of hardening was practically the same whether the alloy was held at a constant temperature or allowed to cool slowly. For example, cooling the alloy from 450° C. (840° F.) to 250° C. (480° F.) in 30 minutes produced practically the same effect as heating at 450° C. (840° F.) for 30 minutes. These findings were verified by tests of the various mechanical properties. A description of these tests and further

details of the effects of heat treatment are given in a following section on mechanical properties.

From the standpoint of practical application in the dental laboratory the method of hardening by slow cooling has two very marked advantages in that when this method is employed it is not necessary to know so precisely the temperature most suitable for hardening a given alloy nor to measure the temperature of the work very accurately during the heat treatment. This method was therefore adopted as standard for this investigation and used for all alloys except those for which special heat treatments were recommended by their manufacturers. The rate of cooling found most efficient for this purpose was the rate obtained by allowing the specimen to cool from 450° C. (840° F.) to 250° C. (480° F.) in 30 minutes.

There has been some ambiguity in the terms used in the dental literature to describe the heat treatments of gold alloys. The quenching operation, by which these alloys are softened, has often been referred to as "annealing" although, as generally used, this term implies a slow rate of cooling, and the hardening treatment has been called "tempering," a term which, as applied to steel, means a slight softening of the hardened alloy by heating. In order to avoid such ambiguity, the terms "softening heat treatment" and "hardening heat treatment" are used throughout this paper and are defined as follows:

Softening heat treatment.—The heating of the specimen to 700° C. (1,290° F.) and quenching in water. In the case of specimens of the size used in dentistry this treatment will soften the alloy whether it has been hardened by mechanical working or by previous heat treatment.

Hardening heat treatment.—The gradual cooling of the specimen from 450° C. (840° F.) to 250° C. (480° F.) over a period of 30 minutes.

In the case of certain alloys variations from these rates of cooling are permissible and sometimes produced more desirable properties. Thus, for some alloys air cooling from 700° C. (1,290° F.) will produce a condition almost as soft as that produced by quenching, while for others air cooling will produce a marked hardening effect. Those alloys that are decidedly hardened by air cooling may become quite brittle if cooled from 450° C. (840° F.) to 250° C. (480° F.) in 30 minutes, and greater ductility may be obtained by cooling at a faster rate. However, for practical purposes the maximum softening and hardening effects may be obtained by the treatments specified above.

A consideration of the heating devices used by some technicians and demonstrators for carrying out these heat treatments leads to the conclusion that some of the devices employed are totally inadequate. In some cases these heat treatments are attempted

using only an open gas flame or an electric hot plate while in others an inclosed box type electric oven, such as the one illustrated in Figure 14, is used.

In the case of small pieces of wire or plate, such as are ordinarily used in the construction of dental applicances, the heating preliminary to quenching for the softening treatment may be done successfully over a gas flame, provided care is taken to heat the work as uniformly as possible and to avoid overheating. An experienced technician may judge the temperature with sufficient accuracy by observing the color of the work. However, a much safer and more reliable method is to use a properly designed electric furnace provided with a pyrometer. For the hardening heat treatment, which requires that the work be held at a definite temperature for a definite length of time or that it be cooled at a definite rate, the open flame is obviously inadequate.

The temperatures at various distances above an electric hot plate and above the shelf of an inclosed box type electric oven are recorded in Table 4. When it is remembered that a dental appliance supported on a hot plate would ordinarily extend at least 5 to 10 mm above the plate, it is obvious that the temperature variations from one part of the appliance to another would be so great that the appliance could not be hardened uniformly. Furthermore, no means is provided for measuring the temperature of the work or for allowing the work to cool slowly. The hot plate, therefore, is not a suitable heating device for carrying out this heat treatment.

TABLE 4.—*Comparative temperature gradient above hot plate and inclosed shelf of oven*

Distance above plate or shelf	Temperature			
	Above hot plate		Above shelf	
	° C.	° F.	° C.	° F.
Contact	460	860	640	1,184
5 mm	175	347	550	1,022
10 mm	125	257	515	959
25 mm	120	248	420	788

As will be seen from Table 4 the temperature above the shelf of the inclosed box-type oven is much more uniform. Further advantages of such a device are that it can readily be equipped with a rheostat for temperature control and a thermometer or other suitable device for measuring the temperature. Such a heating device when properly equipped and standardized has proved very satisfactory for hardening short specimens. For heat treating long test specimens the equipment shown in Figure 15 was used. The temperature

in this furnace is very uniform and can be measured and controlled accurately.

It should be noted that the purpose of this investigation of the heat treatment of dental gold alloys was to develop efficient and practicable methods. No attempt was made to develop a theoretical explanation of the effects produced on the mechanical properties. Several authors of articles appearing in dental journals have stated that the hardening of these alloys, due to heat treatment, is caused by the formation of intermetallic compounds of gold and copper. Apparently these statements are based on the results of the extensive investigation of the binary alloys of gold and copper by Kurnakow,[8] Zemczuzny, and Zasedatelev. While it seems probable that these statements are at least partly correct, it should be borne in mind that most of the dental gold alloys contain metals other than gold and copper, and that in some cases these other metals appear to have a marked influence on the hardening effect. A thorough investigation of the cause or causes of the hardening of the complex dental gold alloys, resulting in authoritative information on this subject, should prove a valuable contribution to the science of dental metallurgy.

(e) MECHANICAL PROPERTIES

As was stated in a previous section, the suitability of an alloy for any mechanical use should be judged principally by its mechanical properties. For this reason in the investigation of the wrought gold alloys the major part of the work was devoted to the determination of the mechanical properties of the various alloys and the possibility of improving these properties by heat treatment. Most of the conclusions are drawn from the results of these tests.

The mechanical properties investigated were resistance to flexure, tensile properties, Brinell hardness or resistance to indentation, and resistance to alternating bending stresses. In all cases the tests were made on samples of a size commonly employed in dentistry. A description of the apparatus and methods used in making these tests and of the results obtained follow.

(1) STATIC FLEXURE TEST (FRANCKE MACHINE).—The instrument used in making these tests was invented by the late W. J. Francke, of New Brunswick, N. J., and is fully described in a paper by Mr. Francke.[9] The instrument is shown in Figure 16. A brief description of the test follows. One end of the sample under test is fastened in jaws, *J*, and the other carries a contact-indicating device, *C*. A pan and weight are added at *W*. The weight causes a deflection of the specimen, which is measured with the micrometer. If the point

[8] Kurnakow, N.; Zemczuzny, S.; and Zasedatelev, M., "The transformations in alloys of gold with copper," J. Inst. of Metals, London, 15 p. 305; 1916.

[9] Proc. Am. Soc. for Testing Materials, 20, p. 372; 1920.

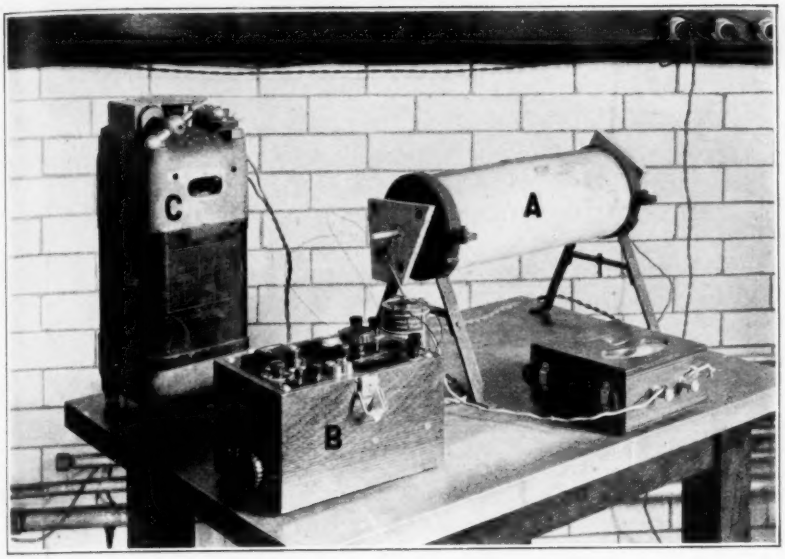

FIG. 15.—*Apparatus for heat treating long wire test specimens*

A, Electric furnace; *B*, Potentiometer and thermocouple used for measuring temperature; *C*, Voltage regulator for controlling temperature.

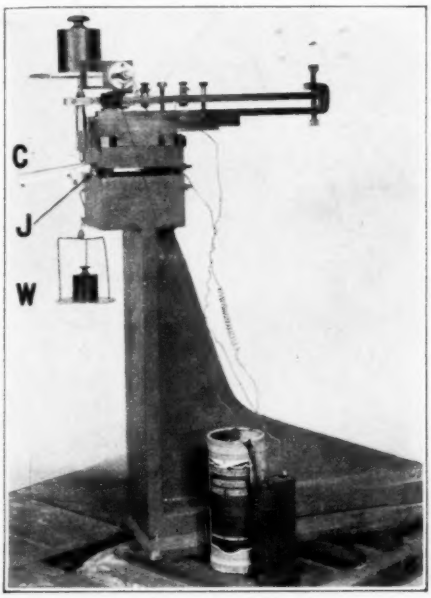

FIG. 16.—*Francke machine for static flexure tests*

of the micrometer and the contact indicating device do not meet at the axis of the specimen, a correction must be applied to the observed deflection in order to obtain the true deflection. After the deflection is measured the weight is removed and the return of the sample is measured with the micrometer. The difference between the deflection and the return is the set or permanent deformation. By using samples of uniform dimensions and increasing the load by small increments it is possible to obtain relations between load, deflection, and set that furnish a basis of comparison of the different alloys, the effects of heat treatment, and other factors.

The samples used in this test were round wires 0.035 inch in diameter, and the effective length or the distance from the jaws to the point at which the load was applied was one-half inch. In order to eliminate variations in the size of wires of different manufacture all wires were purchased as No. 19 gauge (0.036 inch) and drawn to 0.035 inch in diameter through a diamond die.

This test was used as a check on the thermal emf method, described in a previous section, in establishing the proper heat treatments for the various alloys. The values obtained for some of the heat treatments given a single alloy (alloy A) are given in Table 5, and a summary of the values for all the wires tested is presented in Table 6. In all cases at least three duplicate samples were tested and the average value reported. The relations between load, deflection, and set for two alloy A wires, one given the softening heat treatment and the other the hardening heat treatment, are represented graphically in Figure 17.

TABLE 5.—*Effect of heat treatments on mechanical properties of alloy A*

Heat treatment	Deflection causing set of 0.005 inch	Load (A) causing set of 0.005 inch	Load (B) causing set of 0.010 inch
	Inch	*Pounds*	*Pounds*
Hard drawn	0.0385	1.32	1.54
325° C., 10 minutes, quenched twice	.0730	1.65	1.87
450° C., 10 minutes, quenched	.0785	1.76	
600° C., 2 minutes, quenched	.0685	1.54	1.65
700° C., 2 minutes, quenched	.0420	.88	.99
800° C., 2 minutes, quenched	.0480	.88	.99
700° C., quenched 325° C., 10 minutes, furnace cooled	.0560	1.21	1.32
700° C., quenched 320–410° C., 30 minutes, air cooled in pan	.0510	1.10	1.27
700° C., quenched 400° C., 5 minutes, furnace cooled	.0600	1.21	1.38
700° C., quenched 450° C., 5 minutes, furnace cooled	.0630	1.49	1.65
700° C., quenched 450° C., 5 minutes, air cooled in pan (room temperature in 2½ minutes)	.0570	1.27	1.38
700° C., quenched 500° C., 20 minutes, furnace cooled 20 minutes	.0520	1.21	1.38

TABLE 6.—*Results of flexure tests (Francke)*

Alloy	Deflection causing set of 0.005 inch	Load (A) causing set of 0.005 inch	Load (B) causing set of 0.010 inch	B-A
	Inch	*Pounds*	*Pounds*	*Pounds*
A Softened	0.0400	0.88	0.99	0.11
A Hardened	.0510	1.21	1.43	.22
B Softened	.0335	.66	.77	.11
B Hardened [1]	.0595	1.21	1.54	.33
C Softened	.0500	.99	1.21	.22
C Hardened	.0600	1.43	1.76	.33
D Softened	.0455	.99	1.21	.22
D Hardened	.0490	1.10	1.32	.22
E Softened	.0360	.77	.94	.17
E Hardened	.0385	.88	1.10	.22
F Softened	.0385	.77	.99	.22
F Hardened	.0510	1.21	1.43	.22
G Softened	.0380	.99	1.21	.22
G Hardened	.0475	1.16	1.43	.27
H Softened	.0390	.88	1.05	.17
H Hardened [1]	.0439	.99	1.21	.22
H Hardened	.0630	1.49	1.82	.33

[1] Air cooled from 700° C.

The values reported in Tables 5 and 6 are the deflection and load corresponding to a permanent set of 0.005 inch and the load necessary to produce a set of 0.010 inch. In Table 6 the difference between the load necessary to produce a set of 0.010 inch and that necessary to produce a set of 0.005 inch is given also. The load required to cause a set of 0.005 inch may be considered as an index of the stress to which the wire may be subjected without serious injury or without causing it to lose its shape. This is equivalent to the maximum force the wire may be made to exert without being permanently deformed when used as a spring. The deflection caused by this load is the distance through which the spring will exert force and one-half the product of these two (force times distance) is the work the spring will do or its resiliency. The difference between the load necessary to cause a set of 0.005 inch and that to cause a set of 0.010 inch furnishes a basis for judging the relative manipulative qualities of the wires. If the difference is small, it indicates that, after an initial set (0.005 inch) has been produced, an additional load causes a relatively large deformation, or the wire is easily manipulated. If the difference is large, it has been found that in most cases the wire is brittle and will break readily when a large deformation or sharp bend is attempted.

Referring to Table 5, it will be noted that quenching alloy A from 600° C. (1,110° F.) or lower temperatures not only does not soften, but the heat treatment incident to the operation actually hardens or increases the resistance to flexure of the hard-drawn wire, as is evidenced by the increased load necessary to cause a permanent set of 0.005 inch. Quenching from 700° C. (1,290° F.) or over produced the greatest softening effect. Other tests not included in this table

seemed to indicate that quenching from temperatures higher than 800° C. (1,470° F.) is not desirable because of a slight deterioration in the mechanical properties of the alloy. In the lower part of the table values are given showing the effect of additional heat treatment after quenching from 700° C. (1,290° F.). Heating to temperatures below 300° C. (570° F.) had little, if any, effect. Heating at temperatures ranging from 325° to 500° C. (615° to 1,110° F.) or slow cooling from these temperatures had a marked hardening effect, the magnitude of the effect increasing as the temperature was raised to

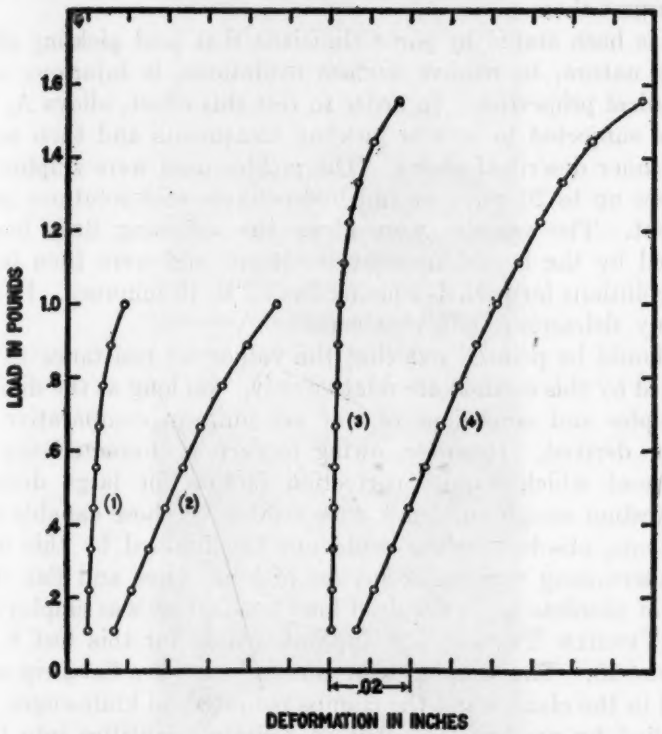

FIG. 17.—*Graphical representation of results of static flexure tests*

(*1*) and (*2*) represent the permanent set and total deformation, respectively, of a sample of alloy A softened; (*3*) and (*4*) represent the permanent set and total deformation, respectively, of a sample of alloy A hardened.

450° C. (840° F.) and also as the rate of cooling was decreased. The maximum effect was obtained by cooling from 450° C. (840° F.) to room temperature in about three hours, this being the slowest rate of cooling employed. As the temperature was raised above 450° C. (840° F.) no additional hardening was noted when the alloy was cooled slowly, and when it was held at a constant temperature the effect was decreased. These findings were verified by similar tests on other alloys. The rate of cooling adopted was from 450° C. (840° F.) to 250° C. (480° F.) in one-half hour, as it was found that

slower rates gave only very slightly increased effects unless a rate so slow as to be impracticable was used.

By referring to Table 6 it will be noted that all the wires in this group were tested in both the softened and hardened conditions. The heat treatments, except in the case of alloy B, hardened, and one series of alloy H wires, were those defined in the section on heat treatment. The two alloys mentioned were hardened by air cooling from 700° C. (1,290° F.), as this treatment corresponds to the recommendations of their respective manufacturers in so far as we were able to interpret them.

It has been stated by some clinicians that acid pickling of alloys of this nature, to remove surface oxidations, is injurious to their mechanical properties. In order to test this effect, alloys A, E, and F were subjected to several pickling treatments and then tested in the manner described above. The pickles used were sulphuric acid solutions up to 20 per cent and hydrochloric acid solutions up to 33 per cent. The samples were given the softening heat treatment followed by the hardening heat treatment and were then boiled in these solutions for periods ranging from 2 to 10 minutes. In no case was any deleterious effect detected.

It should be pointed out that the values for resistance to flexure obtained by this method are relative only. So long as the dimensions of samples and conditions of test are uniform comparative values may be derived. However, owing to certain characteristics of the instrument which require correction factors for large deflections, when testing samples of small cross section, or those capable of large deflections, absolute values could not be obtained by this method. For determining various properties of both wires and flat stock in terms of absolute units the dead load tensile test was employed.

(2) Tensile Tests.—The apparatus used for this test is shown in Figure 18. The sample, either a round wire or a flat strip or band, is held in the clamps and the clamps mounted on knife-edges. Load is applied by pouring lead shot in definite quantities into the pail suspended from the lower end of the sample. The extensometer shown in the figure indicates the deformations by means of the dial micrometer. The extensometer illustrated was used for wires. A modification of this employing two dial micrometers, one on each flat side, was used for strips. Loads and the corresponding deformations were recorded in the usual manner until a stress well above the proportional limit was reached. The extensometer was then removed and loads applied until the sample failed.

All wires tested were purchased as No. 19 gauge (0.036 inch in diameter) and drawn through the 0.035 inch diamond die previously mentioned. The strips were purchased as 0.23 inch wide and 0.006 inch thick. The variations in dimensions were determined by meas-

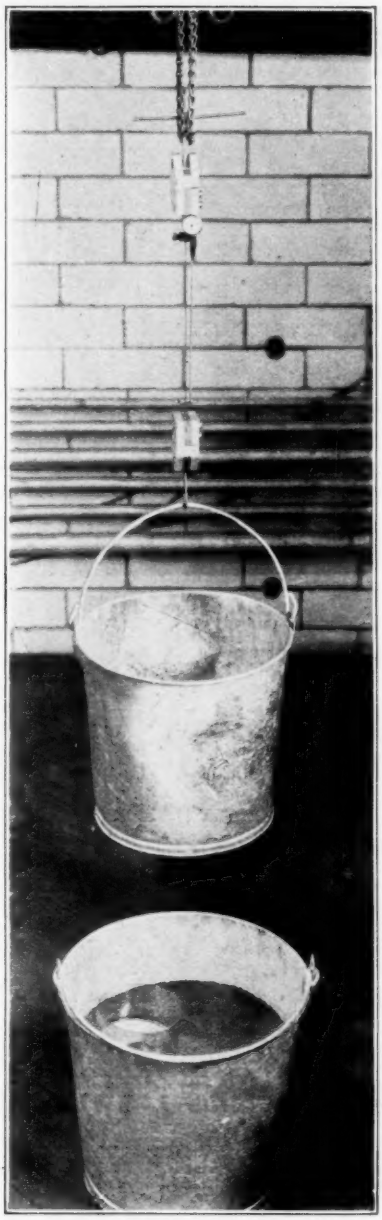

FIG. 18.—*Equipment for making dead-load tensile tests on wires and strips*

uring each strip at several points. All samples, except where otherwise stated, were 12 inches long and the gauge length over which deformation was measured was 8 inches. The errors in the loads did not exceed 0.1 per cent, and errors in the readings of the extensometer did not exceed 0.0002 inch. Tests were made on at least three duplicate samples for each heat treatment of each alloy and the average value for each heat treatment reported.

Definitions of the properties determined by this test are listed below. Brinell hardness also is defined at this time because it is closely associated with the tensile properties. A brief discussion of the practical significance of these properties is included.

Proportional limit.—The stress at which the deformation as determined by the extensometer ceases to be proportional to the load. In the case of the wrought alloys tested, it was found that deformation was not strictly proportional to stress even for very low stresses. In these tests the load increments were uniform and the proportional limit was taken as that stress at which the next increase in load caused an increase in deformation exceeding the previous mean increment by 10 per cent. For practical purposes this may be regarded as the stress at which the initial permanent deformation occurs. Remembering that when a clasp, bar, or similar appliance is distorted or bent out of its proper shape by the forces to which it is subjected in use, certain parts of the appliance are subjected to tensile stress, it is readily seen that the proportional limit of the material of which the appliance is made is an index of the ability of the appliance to maintain its proper shape in service. It is equally true that the proportional limit is an index of the resistance of the material to bending or adjusting to the desired shape.

Ultimate strength.—The stress causing rupture of the specimen. This is an index of the stress an appliance will withstand without failing due to breakage.

Elongation.—The increase in length measured after rupture expressed in percentage of the original gauge length. The elongation is an index of the extent to which the material may be permanently stretched or bent before failure. This property has a direct bearing on the suitability of materials for making appliances that must be bent, swaged, or burnished to shape.

Modulus of elasticity.—Ratio of stress within the proportional limit to the corresponding strain or deformation. It is a measure of stiffness or the force required to produce a given elastic deformation.

Modulus of resiliency.—The potential energy stored up in unit volume of material stressed to the proportional limit. The value depends upon the proportional limit and the modulus of elasticity and is a measure of the work the material can do with safety when used as a spring.

Brinell hardness.—Ratio of load on a sphere used to indent the material tested to the area of the spherical indentation produced. Usually the hardness number is derived from measurements of the diameter of the indentation, from which the spherical area can be computed. It is an index of the resistance of the material to indentation and should be considered in selecting suitable materials of which to make crowns, inlays, or other appliances which are to be subjected to direct stresses such as may be set up by the cusps of opposing teeth.

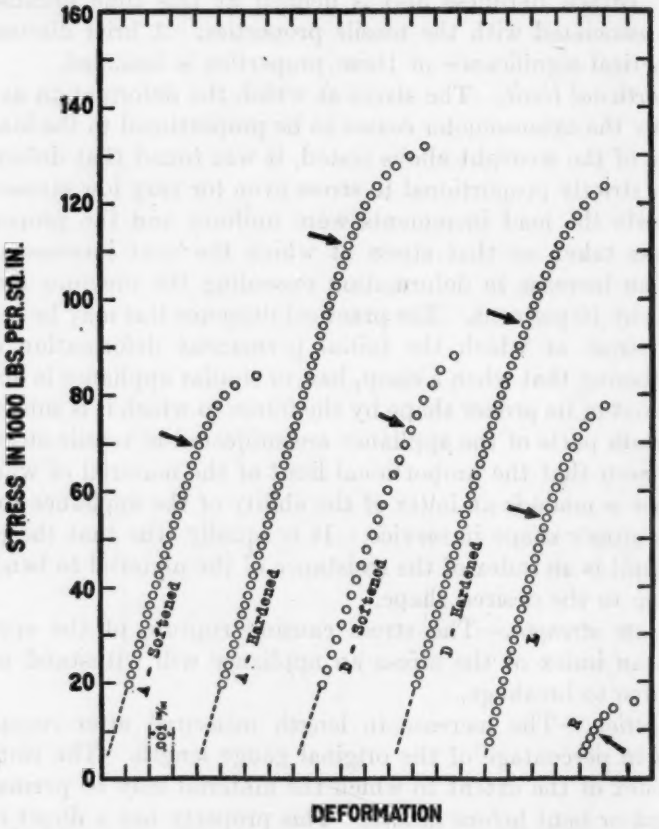

FIG. 19.—*Stress-strain curves derived from tensile tests of wrought gold alloys*

Proportional limits are indicated by the arrows

The values obtained for all wires and strips tested are summarized in Tables 7 and 8. The stress-strain relations for four wires, A softened, A hardened, D softened, and D hardened, and two strips, *L* and *R*, are shown graphically in Figure 19.

By referring to Table 7 it will be noted that the hardening heat treatment caused an increase in proportional limit and tensile strength for all wires tested except alloy G. The hardening heat treatment

previously described was employed for all of these alloys except alloy B and one series of alloy H. These were given the treatment recommended by their respective manufacturers, namely, cooling in air from approximately 700° C. (1,290° F.). The wires developing the highest tensile strengths in the hardened condition were alloys H, C, and A in the order named. Of these, alloy A, with an ultimate strength of 153,000 lbs./in.[2], had the highest elongation, 7.5 per cent in 8 inches. This was the highest elongation of any hardened wire tested, with the exception of alloy H, air cooled from 700° C (1,290° F.), which developed a much lower ultimate strength.

TABLE 7.—*Tensile properties of wire* [1]

Alloy	Proportional limit		Ultimate strength		Elongation in 8 inches	Modulus of elasticity	Modulus of resiliency
	Pounds	*Lbs./in.*[2]	*Pounds*	*Lbs./in.*[2]	*Per cent*	*Lbs./in.*[2]	*In.lbs./in.*[3]
A Softened	68	71,000	104	108,000	12.5	17,000,000	147
A Hardened	106	110,000	148	153,000	7.5	18,000,000	332
B Softened	62	64,000	90	94,000	11.0	17,000,000	119
B Hardened [2]	84	87,000	119	124,000	3.6	17,000,000	223
C Softened	81	84,000	119	124,000	9.6	18,000,000	193
C Hardened	128	133,000	168	175,000	4.6	19,000,000	473
D Softened [3]	71	74,000	104	108,000	8.8	14,000,000	201
D Hardened [2]	92	96,000	132	138,000	1.0	17,000,000	278
E Softened	61	63,000	97	102,000	10.2	16,000,000	122
E Hardened	73	76,000	118	123,000	6.8	17,000,000	172
F Softened	66	69,000	98	102,000	9.2	17,000,000	138
F Hardened	75	78,000	113	118,000	6.0	16,000,000	187
G Softened	77	80,000	121	126,000	2.9	20,000,000	162
G Hardened	79	82,000	118	123,000	3.2	21,000,000	162
H Softened	76	79,000	109	113,000	10.6	17,000,000	186
H Hardened [2]	83	86,000	125	130,000	8.4	16,000,000	228
H Hardened	116	121,000	169	176,000	.5	18,000,000	402

[1] All wires of 0.035 inch diameter.
[2] Air cooled from 700° C.
[3] 10 inches total length; 6 inches gauge length.

TABLE 8.—*Tensile properties and hardness of band and plate material* [1]

Alloy	Proportional limit	Ultimate strength	Elongation in 8 inches	Modulus of elasticity	Modulus of resiliency	Brinell hardness number	U. T. S.[2] / B. H. N.[3]
	Lbs./in.[2]	*Lbs./in.*[2]	*Per cent*	*Lbs./in.*[2]	*In.lbs./in.*[3]		
I Softened	58,000	98,000	12.1	16,000,000	103	155	0.63
I Hardened	116,000	157,000	4.6	18,000,000	384	230	.68
J Softened	56,000	90,000	10.1	15,000,000	102	145	.62
J Hardened	89,000	118,000	2.2	16,000,000	249	185	.64
K Softened	57,000	94,000	19.2	17,000,000	94	140	.67
K Hardened	69,000	104,000	15.5	18,000,000	132	150	.69
L Softened	50,000	88,000	4.6	20,000,000	62	145	.61
L Hardened	54,000	91,000	3.7	21,000,000	70	150	.61
M Softened	31,000	86,000	9.9	16,000,000	31	140	.61
M Hardened	44,000	90,000	10.6	15,000,000	54	140	.64
N Softened	25,000	59,000	18.8	13,000,000	23	85	.69
N Hardened	29,000	60,000	15.6	14,000,000	30	90	.67
O Softened	21,000	55,000	28.9	13,000,000	17	90	.61
O Hardened	21,000	54,000	26.2	13,000,000	17	90	.60
P Softened	13,000	48,000	23.9	14,000,000	6	70	.69
P Hardened	13,000	48,000	20.0	17,000,000	5	65	.74
Q Softened	11,000	37,000	17.5	12,000,000	5	60	.62
Q Hardened	12,000	38,000	19.6	12,000,000	6	60	.63
R Softened	9,000	35,000	23.7	10,000,000	3	50	.70
R Hardened	10,000	35,000	20.5	11,000,000	4	55	.64

[1] All specimens were approximately 0.23 by 0.006 inch.
[2] Ultimate tensile strength in 1,000 lbs./in.[2]
[3] Brinell hardness number.

Values for a series of alloy H wires given the standard hardening heat treatment are included in Table 7 for the purpose of illustrating the effect of the rate of cooling. It will be noted that both the proportional limit and the ultimate strength are greatly increased by the slower cooling, while the elongation drops from 10.6 per cent for the quenched and 8.4 per cent for the air cooled to only 0.5 per cent. The other alloys tested were found to be affected in the same way, though to a smaller degree.

Alloy G was not susceptible to hardening by any of the heat treatments tried. This may be due in part to the low copper content. It will also be noted that the modulus of elasticity of alloy G is higher than that of any other alloy in this group. A possible explanation of this lies in the fact that this allow contains an appreciable amount of iridium and is low in copper. This may also account for its low elongation.

By referring to Table 8 it will be noted that alloy I is affected by heat treatment to a marked degree. Alloys J and K are affected to a smaller degree. The remaining alloys of this group are not affected appreciably. The modulus of elasticity of alloy L is high, possibly due to its iridium content. In the case of alloys of very low strength, particularly Q and R, the proportional limit could not be determined with the highest degree of accuracy owing to the limited range of stresses over which observations could be made. The values reported are the best that could be obtained with the equipment available but probably are slightly higher than they should be. This would account for the low values for modulus of elasticity. The importance of these alloys, Q and R, was not considered sufficient to warrant the construction of apparatus for determining these values with greater precision.

(3) Brinell Hardness.—The instrument [10] used for making these determinations is a modification of the standard Brinell hardness tester and was designed especially for testing small samples. A photograph of the instrument is shown in Figure 20. The ball is hardened steel 1.6 mm ($\frac{1}{16}$ inch) in diameter, and for the wrought alloys a load of 6.4 kg (14.1 pounds) was used. This combination is equivalent to a 10 mm ball and 250 kg load. The samples used for this test were strips approximately 0.23 inch wide and 0.006 inch thick. While samples of these dimensions are too thin for the determination of hardness with the highest degree of accuracy, the values obtained bear a definite relation to the true hardness and are comparable. Tests of several alloys using supporting anvils varying in hardness from that of hardened steel to that of bronze indicated that this factor had no appreciable influence on the values

[10] Goodale, S. L., and Banks, R. M., "Development of Brinell hardness tests on thin sheet brass," Proc. A. S. T. M., **19** (pt. 2), p. 757; 1919.

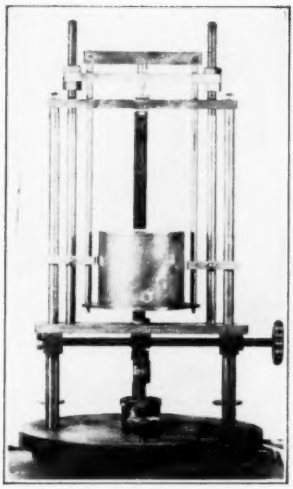

FIG. 20.—*Instrument for determining Brinell hardness of small samples*

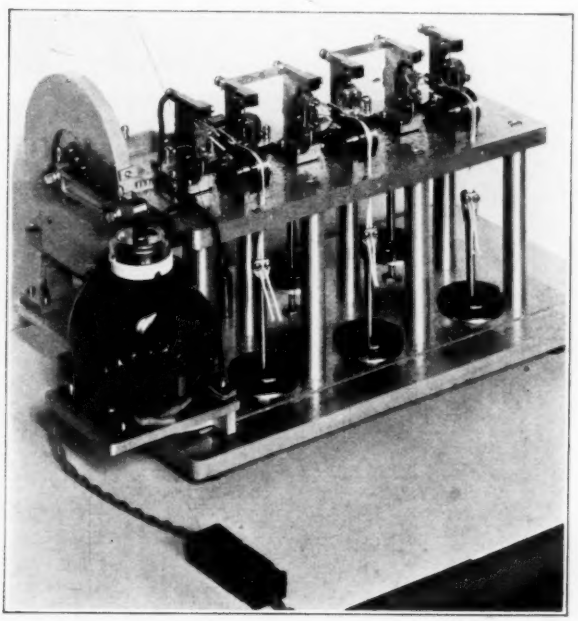

FIG. 21.—*Dead-load flexure machine for making tests of the relative life of alloys subjected to repeated stresses*

obtained. The Brinell harness numbers of all strips tested, in both the softened and hardened states, are given in Table 8. Hardness determinations were also made on all strips as purchased, as a matter of record. As these values are thought to be of little importance to the dentist, they are not included in this report.

The ratio, ultimate tensile strength in 1,000 lbs./in.^{2} divided by Brinell hardness number, is also given in Table 8. From these values the relation between these two properties for alloys of this group, excepting only alloy P hardened, may be written as $S = (0.65 \pm 0.05)H$, where S is tensile strength in 1,000 lbs./in.^{2} and H is Brinell hardness number.

(4) Life Tests (Repeated Stresses).—It is well known to many dentists that clasps, both wrought and cast, orthodonthia spring wires, and other appliances that are subjected to repeated stresses, such as those induced by mastication or the removal and insertion of the appliance in the mouth, often give good service for a time but eventually fail, due to breakage, even when there is no evidence that the appliance has been subjected to abnormal usage or abuse. Such failures have been attributed to "crystallization" and numerous other causes, but are now generally recognized as being due to fatigue or the effect of stress applied a great number of times. It appeared desirable, therefore, to obtain some data on the relative resistance of the various dental gold alloys to these repeated stresses.

Although a great deal of data on the fatigue resistance of a number of ferrous and nonferrous alloys had been published, no report of such data on dental gold alloys was found in the literature. None of the machines commonly employed in determining fatigue resistance appeared to be entirely suitable for testing samples of the size used in dentistry. It was necessary, therefore, to design and construct a special machine for this investigation. In designing this machine valuable advice and assistance was received from the staff of the bureau's laboratory of engineering mechanics and other members of the bureau's staff familiar with fatigue testing. A number of designs were suggested and rejected because of defects. A photograph of the machine built according to the design finally adopted is shown in Figure 21.

A brief description of the operation of this machine follows. The sample under test is supported in a horizontal position between one of the three pairs of upright holders shown at the top of the photograph. A yoke is placed over the sample midway of the holders, and cords fastened to either side of the yoke pass over pulleys and support weights. These weights are lifted alternately by means of a rocker arm driven by the motor shown at the left of the photograph. As the weight on one side is lifted the one on the other side is allowed to hang suspended from the sample under test. Thus the sample is subjected to a bending stress first in one direction and then in the

other. The magnitude of the stress can be varied at will by adjusting the weights. The number of applications of stress is recorded by means of a revolution counter, and the operation is continued until the test specimen fails.

The fatigue resistance of a material is usually expressed as the maximum stress which a specimen will endure for any number of repetitions, or as the stress at which the specimen endures a definite number of alternations of stress. In order to determine these values it is necessary to test specimens at each of a number of stresses, a procedure which would require a great deal of time, especially with a low-speed machine, such as the one used in this investigation. For this reason it was decided to use as an index of the relative fatigue resistance, or life, of the dental gold alloys of this group the number of alternations of a definite stress endured by each alloy. Accordingly a load was selected that would cause failure of most of the alloys between 10,000 and 100,000 reversals.

The specimens used were round wires 0.035 inch in diameter, accurately sized by drawing through the diamond die previously mentioned. The length of the specimen between supports was 2 inches, and the load used was 14 ounces. With this combination the theoretical maximum fiber stress set up in the test specimen was calculated to be approximately 100,000 lbs./in.^{2} The selection of a markedly different stress value will undoubtedly change slightly the relative arrangement or order of failure, but such changes as are necessary to produce an arrangement differing appreciably from that reported do not appear to be justified from service conditions.

At least three duplicate samples of each material were tested and the average value reported. The values obtained are given in Table 9. These indicate a marked variation in the life or length of service to be expected of the different materials. It will be noted that for all alloys, except alloy G, tested in both the softened and hardened conditions, the life value is greatly increased by the hardening heat treatment. As the other mechanical properties of alloy G were not susceptible to improvement by heat treatment, it was not expected that such treatment would greatly affect its life value. In the case of alloy A, however, the useful life was increased fivefold. This furnishes a very striking example of the benefits to be derived from properly heat treating alloys of this character.

TABLE 9.—*Results of flexure life tests: Number of reversals to cause failure*[1]

	Alloy							
	A	B	C	D	E	F	G	H
Softened	15,000	4,000	23,500				19,000	41,000
Hardened	75,000	15,000	88,500	23,500	18,000	25,000	24,000	58,000

[1] Average of several tests given to nearest 500.

2. CAST ALLOYS

(a) CHEMICAL COMPOSITION

As a preliminary survey of the field, in order to determine something of the general nature and variations likely to be encountered in dental casting golds, chemical analyses were made of a number of selected alloys. The analyses were made by William H. Swanger, research associate, and Dr. R. Gilchrist, chemist, Bureau of Standards. The methods [11] employed in analyzing these alloys were the same as those used in connection with the wrought alloys. The chemical compositions, together with the uses recommended for these alloys by their respective manufacturers, are given in Table 10. In many instances the properties of the alloys as stated by their manufacturers are also included.

Alloys XXVII, XXVIII, XXIX, XXX, S-III, S-IV, and S-V were made up by the cooperating laboratories as being representative of various grades of material as indicated in the table. In the case of the solders it should be noted that they are representative of the higher gold content solders employed for the purposes indicated. Of this group only one, alloy XXVIII, was analyzed. The analysis and batch formula of this alloy agreed within the limits of accuracy of the analysis. The compositions reported for this group of alloys are the batch formulas.

TABLE 10.—*Chemical composition of casting golds (per cent by weight)*

Alloy	Gold	Silver	Copper	Platinum	Palladium	Nickel	Zinc	Iridium	Tin	Uses and claims as stated by manufacturers
I	71.3	7.1	9.9	10.62	.....	.....	0.08	0.14	0.83	For casting clasps and bars; extra hard; gold color; melting point, 1,750° F.
II	78.0	10.0	5.9	6.1	.....	.....	.....	.1	.....	For hard inlays, abutments and three-quarter crowns.
III	60.0	11.0	8.8	13.1	5.94	.....	.72	.10	.14	For cast clasps; melting point, 1,960° F.; platinum color.
IV	71.4	6.0	15.6	2.78	.....	1.98	2.38	.....	.....	For clasps, saddles, arches, and bars; for casting clasps and saddles in one piece; very tough, strong, and springy; fusing point, 1,870° F.
V	62.8	13.9	18.9	.....	.....	2.57	1.92	.....	.....	For clasps, saddles, bars, etc.; one-piece castings.
VI	59.3	8.1	12.7	15.95	3.55	.....	.08	.....	.....	For cast clasps; 21 per cent plat.
VII	59.8	13.5	13.6	5.22	7.10	.....	.67	.20	.....	For clasps; 14 per cent plat.
[1] VIII	65.9	5.9	10.2	10.58	5.69	.....	1.34	.03	.....	A cast-clasp alloy containing gold, platinum, palladium, and rhodium; high elasticity and strength; melting point, 2,105° F.
IX	64.9	12.5	10.0	12.23	.....	.....	.03	.14	.1	For clasps, bars, crown posts, bridge construction, soldered or cast; tough and springy.
X	68.3	11.1	13.9	2.86	2.89	.93	.05	.....	.....	For clasps, lingual and palatal bars and saddles; gold color; fusing point, 1,800° F.
XI	64.4	7.2	10.4	11.15	5.74	.16	1.07	.....	.....	Cast-clasp metal; unexcelled in strength; high platinum percentage.
XII	65.4	5.4	11.8	10.80	5.64	.05	1.09	.....	.....	Cast clasp metal; excellent for white clasp work; rich in platinum.

[1] Manganese present, but less than 0.01 per cent. Rhodium present, 0.56 per cent, about one-third of which appeared not to be alloyed with the rest of the metal.

[11] See footnote 4, p. 869.

TABLE 10.—*Chemical composition of casting golds (per cent by weight)*—Continued

Alloy	Gold	Silver	Copper	Platinum	Palladium	Nickel	Zinc	Iridium	Tin	Uses and claims as stated by manufacturers
XIII	72.0	9.8	8.8	7.92	.....	0.95	0.15	0.07	.....	For clasps, bridges, etc.; fuses, 1,730° F.; a scientific casting gold.
XIV	66.3	9.7	12.9	2.06	7.78	.....	1.18	.07	.....	For cast clasps, etc.
XV	75.6	.....	10.6	10.14	.....	2.73	1.08	.....	.....	For cast clasps, bars, and saddles requiring spring; extreme strength; melting point, 1,820° F.
XVI	67.8	11.7	10.5	10.12	.....	.....	.....	.....	.....	For cast clasps, long bars, hard attachment retainers, and partial plates; very hard, strong, and springy; melting point, 1,825° F.
XVII	67.0	16.8	12.2	3.92	.....	.....	.....	.05	.....	Gold-platinum-palladium alloy; 6 per cent platinum-palladium; for inlays, clasps, saddles, abutments, etc.; great tensile strength; very springy like, but not brittle.
XVIII	69.6	18.4	4.1	7.72	.....	.....	.....	.10	.....	For cast crown and bridge work; melts at 1,965° F.
XIX	81.1	11.0	4.0	3.75	.....	.....	.....	.10	.....	For full and three-quarter jacket crowns and abutments; melts at 1,840° F.
XX	76.3	5.1	9.8	8.00	.....	.....	.82	.....	.....	Extra tough; for thin three-quarters; bars and saddles without spring; melting point, 1,814° F.
XXI	79.6	4.5	8.0	7.80	.....	.....	.06	.03	.....	The hardest gold yet produced for the casting of Carmichael's, three-quarter, and full crowns and abutment attachments; fusing point, 1,870° F.
XXII	63.1	10.5	11.9	3.15	9.75	.22	1.68	.....	.....	Strong white platinum alloy for denture casting.
XXIII	81.8	7.2	7.2	3.95	.....	.....	.....	.....	.....	For three-quarter crowns, Carmichael's, etc.; fuses 1,760° F.; a scientific casting gold.
XXIV	67.8	16.5	8.9	2.96	2.82	.....	.94	.08	.....	For casting inlays, three-quarter and full crowns, pontics, etc., where these require double strength.
XXV	83.2	8.4	8.3	.....	.....	.....	.....	.....	0.18	For hard, dense inlays.
XXVI	89.8	.04	10.0	.08	.....	.....	.....	.....	.....	For inlays, etc.
[1] XXVII	91.7	7.8	0.5	.....	.....	.....	.....	.....	.....	22-carat gold; used for cast inlays,
[1] XXVIII	91.7	4.6	3.7	.....	.....	.....	.....	.....	.....	etc.
[1] XXIX	75.0	21.8	3.2	.....	.....	.....	.....	.....	.....	18-carat gold; used for cast den-
[1] XXX	75.0	18.8	6.2	.....	.....	.....	.....	.....	.....	tures, etc.
S–I	65.4	15.4	12.4	.....	.....	.....	3.9	.....	3.1	Solder for 18-carat plate, 656 fine.
S–II	66.1	12.4	16.4	.....	.....	.....	3.4	.....	2.0	Solder for 18-carat plate, 650 fine.
[1] S–III	65.0	16.3	13.1	.....	.....	.....	3.9	.....	1.7	Solder for 18-carat gold.
[1] S–IV	72.9	12.1	10.0	.....	.....	.....	3.0	.....	2.0	Solder for 20-carat gold.
[1] S–V	80.9	8.1	6.8	.....	.....	.....	2.1	.....	2.0	Solder for 22-carat gold.

[1] Composition given is the batch formula.

By referring to Table 10 it will be noted that, as in the case of the wrought alloys, these materials contain small percentages of a large number of metals, as many as nine metals being found in a single alloy. Some of these are undoubtedly present as impurities in the major constituents. The formulas of most of these alloys are quite complex and appear to be largely empiric.

It is thought that the chemical compositions of this great variety of alloys, supplemented by complete tests of a few alloys representative of the various types, furnish a very good index of the general properties of the casting golds in use.

(b) MELTING RANGES

Although the "wire "method [12] of determining fusion temperatures, used in the investigation of wrought alloys, furnishes an index of the

[12] See footnote 7, p. 877.

maximum temperature at which these materials may be manipulated with safety, this method does not yield sufficient information in the case of casting golds and solders. For the most intelligent use of these materials it is necessary to know not only the maximum temperatures at which they are sufficiently rigid and cohesive to be soldered, bent, or otherwise manipulated with safety, but also the minimum temperatures at which they are sufficiently fluid to be cast or, in the case of solders, flowed. For this reason it was necessary to determine the melting ranges of the alloys of this group. The lower limit of the metling range, or the temperature at which fusion begins, is an index of the maximum temperature at which the alloy may be manipulated with safety, and the upper limit, or the temperature at which fusion is completed, is an index of the minimum temperature at which the alloy may be cast or flowed in the case of a solder.

In determining the metling ranges of these alloys the usual method of observing the changes in the rate of heating or cooling as the alloy is melted or allowed to freeze was employed. Two such determinations are illustrated in Figure 12. The melting ranges determined are given in Table 14, in which the mechanical properties also are summarized. By referring to this table it will be noted that the melting ranges of most of the alloys of this group are quite long, in some cases extending over 100° C. or more. Alloy S-V, solder for 22-carat gold, furnishes a striking example of the significance and importance of this range.

Careful determinations of the metling range of this alloy showed that fusion of a small part of its constitutents begins at 745° C. (1,375° F.), although complete liquidation of the alloy does not occur until a much higher temperature is reached. Samples heated to approximately 750° C. (1,380° F.) appeared to be solid upon visual observation but were found to be extremely weak, falling to pieces when picked up with tongs. It is obvious that if this solder is used in the construction of an appliance which later must be soldered at a place near the first joint, care must be taken to use a solder for this operation which is flowed at a temperature below 745° C. (1,375° F.), or other suitable precautions must be taken in order to avoid possible injury to the first joint.

It will be noted that there is quite a large variation in the melting ranges of the various casting alloys examined. The upper limit of the ranges varies from 1,050° C. (1,920° F.) to 870° C. (1,600° F.) and the lower limit from 1,030° C. (1,885° F.) to 820° C. (1,510° F.) for alloys XXVII and V, respectively. The upper limits should be considered in selecting suitable equipment for melting these alloys preparatory to casting. The lower limits, as well as the metling ranges of the solders themselves, should be considered in selecting suitable solders for use in conjunction with the cast appliance.

(c) MECHANICAL PROPERTIES

In the investigation of the mechanical properties of the cast gold alloys the properties determined were proportional limit, ultimate tensile strength, modulus of elasticity, percentage elongation, and Brinell hardness. The effects of heat treatment and of variations in the casting processes were also studied.

In determining these properties, especially the tensile properties, a number of difficulties were encountered. One of the most important of these was the preparation of suitable test specimens. These specimens should be castings of such size and produced under such conditions as to be analagous to dental castings in their properties. At the same time they must be large enough to permit sufficient accuracy in testing. As a preliminary to the development of a method of producing such samples it was necessary to determine as much as possible concerning the properties of dental castings and the variations in properties likely to be produced by variations in the casting process. Accordingly, a number of castings were made and examined to determine the effects of such variations.

In the dental literature mention has been made of the occurrence and deleterious effects of the segregation and burning out of certain constituents of casting golds. Tests were made to determine to what extent these effects are likely to occur in the ordinary dental casting process. A cylindrical casting 10 mm in diameter and about 20 mm long was made of Alloy III, an alloy relatively high in platinum and palladium. Chemical analyses were made of the outside and center of this casting to determine whether or not there was a difference in the compositions of these parts of the casting. As these analyses were made for comparison only, determinations of all the constituent metals were not made. The analyses are given in Table 11. No significant difference was found.

TABLE 11.[1]—*Segregation in Alloy III* [2]

	10 mm casting		Cast at moderate temperature [3]				Cast at high temperature [4]			
			Air pressure		Centrifugal		Air pressure		Centrifugal	
	Outside	Inside	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom
Au.....per cent..	59.9	60.4	59.9	59.9	59.8	60.1	60.3	60.4	60.4	60.6
Ag.....do....	10.9	10.9	10.9	11.0	10.9	10.9	11.0	11.0	11.0	11.1
Cu.....do....	8.8	8.5	.....	.....	.....	.....	.....	.....	8.6	8.8
Zn.....do....	.76	.78	.72	.76	.77	.67	.56	.56	.....	.....
Pt.....do....	12.9	13.4	.....	.....	.....	.....	.....	.....	12.9	12.3
Pd.....do....	.....	.....	.....	.....	.....	.....	.....	.....	5.9	5.8

[1] Analyses were made by W. H. Swanger, research associate, Bureau of Standards.
[2] Complete analyses were not made. The values reported are sufficient for purposes of comparison.
[3] Throughout this report the term "moderate temperature" is used to designate a temperature slightly above the minimum at which castings could be made with the alloy in question. It is obvious that this temperature will vary for different alloys, depending upon their melting points, and, possibly to some extent, on other factors.
[4] The term "high temperature" is used to designate a temperature markedly higher than the moderate temperature defined above.

Two series of castings of Alloy III were then made with both an air pressure and a centrifugal casting machine. For one series the gold was heated to a moderate casting temperature with a hydrogen-air blowpipe. For the other series the gold was heated to much higher temperature with an oxygen-gas blowpipe. The castings were rods approximately ⅛-inch in diameter by 1½ inches long and were made in investment molds at a temperature of about 250° C. (480° F.) to 300° C. (570° F.). Chemical analyses were made of the top or residue button and the bottom of each of these castings. These analyses also are given in Table 11. In no case was any significant difference between the composition of the top and that of the bottom of a casting found.

The freezing range of this alloy is very long, there being a difference of more than 160° C. between the temperature at which freezing begins and that at which solidification is completed. This and the size of the castings and, in one series of castings, the high temperature of the gold are conditions much more favorable to segregation than those usually encountered in dental practice. Since no segregation was detected even under these conditions, it may be concluded that, in general, this effect is not likely to be serious in dental castings.

The extent to which the composition of this alloy, Alloy III, may be changed by the burning out of certain constituent metals during the casting process was determined by another series of tests. A section ¾ of an inch long was cut out of the center of a cast bar ⅜ of an inch in diameter and 6 inches long. This center section was cut into three parts which were analyzed, one after being remelted with hydrogen and air and held at a moderate temperature for two minutes, one after being remelted with gas and oxygen and held at a very high temperature (approximately 1,600° C., 2,900° F.) for five minutes, and one without remelting. During the remeltings borax flux was used freely. The analyses are given in Table 12.

TABLE 12.[1]—*Change in composition of Alloy III due to remelting*

	Not remelted	Remelted at moderate temperature	Remelted at high temperature
Au.....per cent...	60.5	60.5	60.8
Ag.....do....	11.0	11.0	11.0
Cu.....do....	8.5	8.6	8.6
Zn.....do....	.64	.56	.32

[1] Analyses were made by W. H. Swanger, research associate, Bureau of Standards.

The remelting and holding at a moderate temperature for two minutes is a more severe treatment than the gold would ordinarily receive if cast only once. It may be considered as equivalent to remelting and casting at least twice. Yet it will be noted from Table

12 that no significant change in composition owing to this treatment was found. Heating to the excessively high temperature and holding this temperature for five minutes is very much more severe, both as to the temperature and the length of time this temperature was held than is likely to occur in ordinary dental practice. This treatment was so severe that during the entire five minutes small particles were flying off from the molten metal, and the total loss of metal was approximately one-half of the original weight. As will be seen from Table 12, the only change in composition of the alloy subjected to this treatment was the loss of about 50 per cent of the original zinc content.

In order that the conditions of test with respect to the grade of alloy used might be as severe as any likely to be encountered in practice, the tests were repeated using low-grade alloys (approximately 15-carat gold) containing a large percentage of base metals. These alloys were very similar to alloy V, which was the lowest in precious metal content of the alloys analyzed. (See Table 10.) Since alloy V has been criticized as being too low in precious metals to be used in the mouth with safety it is thought that the low-grade alloys used in these tests represent the extreme in this respect. The results of these tests were very similar to those described for alloy III, except that at the very high temperatures the loss of base metals was slightly greater than for alloy III.

The conclusions to be drawn from these results may be stated briefly as follows: Gold alloys such as those tested in this investigation when remelted and cast with reasonable care are not expected to undergo any serious "unbalancing" or change in the proportions of their constituent metals, even if remelted and cast two or three times. This is true even of alloys so low in precious metal content as to be of doubtful value in the mouth. If due precautions are taken to prevent contamination from oxidation or the inclusion of foreign substances, such treatment should not seriously alter the mechanical properties of these alloys. If, however, the alloys are heated to excessively high temperatures loss of base metals is likely to occur.

In examining a number of castings of these alloys it was found that practically all of them were porous or pitted, though to varying degrees. Such porosity was sufficient to cause marked variations in the properties of different castings of the same alloy. In order to eliminate or reduce as much as possible variations due to this condition, a study of the causes of this porosity was undertaken. A number of articles on this subject are to be found in the dental literature. In most of these porosity is attributed to oxidation of the metal or to occluded gases. In order to verify these reports, and to obtain a clearer understanding of the prevailing conditions, it was decided to make an independent investigation.

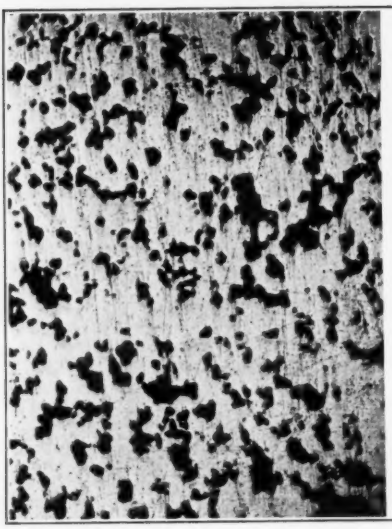

FIG. 22.—*Section of a dental casting polished but not etched, × 90*

Shows type of porosity characteristic of certain casting golds. This appears to be due to localized shrinkage.

FIG. 23.—*Section of a dental casting polished but not etched, × 90*

Shows a second type of porosity characteristic of some casting golds. This appears to be due to occluded gas.

FIG. 24.—*Section of same alloy as shown in Figure 22, after remelting in vacuum. Polished but not etched, × 90*

FIG. 25.—*Section of same alloy as shown in Figure 23, after remelting in vacuum. Polished but not etched, × 90*

Accordingly, a large number of castings were made under systematically varied conditions. The composition of the metals used ranged from 24-carat gold and binary alloys of gold and various other metals to the complex alloys commonly employed in dentistry. The dimensions of the casting and sprue and the method of melting and casting were varied between wide limits. Sections of these castings were prepared and examined for porosity under the microscope.

All of the castings examined were porous to some extent, and in practically all cases the porosity could readily be classified as belonging to one of two apparently distinct types. These types are illustrated in Figures 22 and 23 and appear to be characteristic of certain alloys when melted and cast by any of the methods in common use in the dental laboratory. In Figure 22 the dark spots are voids around or between dendrites. The walls of these voids, when large enough to be seen, are bright and clean. No indication of any discoloration such as would be expected if metallic oxides were present was noted. It was observed, also, that this type of porosity occurs most frequently and is most pronounced in sections of the casting adjacent to the sprue. These characteristics of this type of porosity suggested that the voids were caused by localized shrinkage owing to different rates of cooling in different parts of the casting. In Figure 23 the round, dark spots are voids, the walls of which are also bright and clean. The appearance of these suggested that they were caused by or that their shape was influenced by occluded gas.

As a check on these observations castings of two alloys, which are characterized by these two types of porosity, respectively, were placed in graphite crucibles and packed in zirconia which formed a mold in which the casting could be remelted without losing its original shape. These castings were then remelted[13] in a vacuum-induction furnace, held molten long enough for the elimination of any gas that might be present and allowed to freeze in vacuum. The porosity of these castings was then found to be as illustrated in Figures 24 and 25. The round voids shown in Figure 23 were completely eliminated. Voids similar to those shown in Figure 22 were found in both alloys. The porosity in the vacuum-fused alloys is caused very largely by localized shrinkage, and since this is very similar to the type of porosity shown in Figure 22, which apparently is not caused by metallic oxides or occluded gas, it is concluded that this type of porosity is also caused by localized shrinkage. The elimination of the type of porosity shown in Figure 23 by vacuum fusion, which also eliminates any gas that might be present, tends to confirm the conclusion that this type of porosity is caused by occluded gas.

No evidences of serious porosity, caused by the inclusion of metallic oxides, were found when the usual precautions of melting with a

[13] The remelting in vacuum was done by L. Jordan, of the division of metallurgy, Bureau of Standards.

reducing flame and using a protecting flux, such as fused borax or borax and charcoal, were taken. Determinations [14] of the oxygen and hydrogen present in three alloys, XXIII, XIII, and III as supplied by their respective manufacturers, and in alloy III after being melted under various conditions, are of interest in this connection. The results of these determinations are given in Table 13. The samples tested as manufactured were purchased through a supply house in the usual manner and are believed to be representative of these alloys as supplied to the dental trade. Alloys XXIII and XIII were claimed by their maker to be manufactured by a special process which eliminates the possibility of contamination by oxidation, yet the percentage of oxygen found in these alloys is appreciably greater than that found in alloy III, which is claimed to be manufactured by the usual methods. The values for oxygen and hydrogen content of samples of alloy III melted under three different sets of conditions are given in the lower part of the Table 13, samples 4, 5, and 6. Sample 4 was melted five times on a charcoal block in a hydrogen-air flame and sample 5 was melted once in an air-illuminating gas flame and cast in an investment mold. A flux consisting of powdered carbon and borax was used during the melting of both of these samples. Sample 6 was melted in a refractory crucible in a high-frequency induction furnace and was held completely molten for a period of 1 minute and 20 seconds. No flux or other protective medium was used. After the sample had cooled in the crucible the surface scale was removed by grinding before determining the gas content. In each case the sample used had previously been made gas free by vacuum fusion, hence the gases found were present due to melting under the conditions described.

TABLE 13.—*Gas content of gold alloys*

Sample No.	Alloy	Treatment	Oxygen by weight	Hydrogen by weight
			Per cent	*Per cent*
1	XXIII	As manufactured	0.0026	0.0009
2	XIII	do	.0025	.0007
3	III	do	.0016	.0008
4	III	Originally gas-free metal melted five times in hydrogen-air flame on charcoal block; borax-carbon flux used	.0090	.0019
5	III	Originally gas-free metal melted in air-illuminating gas flame, cast in investment mold; borax-carbon flux used	.0150	.0015
6	III	Originally gas-free metal melted by induction in air without flux; surface scale removed	.038	.0008

It will be noted that the oxygen content of each of these three samples was appreciably greater than that of the alloy as manufactured, indicating that if these alloys are seriously contaminated by oxygen, either in the form of metallic oxides or in some other form, such contamination is much more likely to occur during melting and casting

[14] These determinations were made by L. Jordan, of the Bureau of Standards. For a description of the method used see B. S. Sci. Paper No. 514; 1925.

by the usual dental laboratory methods than in the process of manufacture. The oxygen content of sample 6, which was melted without the protection of a flux or of the products of combustion of a gas flame, was found to be more than twice as great as that of any other sample tested. This furnishes a general indication of the effectiveness of these protective media in preventing contamination of the alloy by oxygen. The oxygen content of sample 5, which received a treatment very similar to that received by the alloy in the usual melting and casting process, was found to be 0.015 per cent by weight. This seems to indicate that only a minor proportion of the porosity usually found in dental castings can be due to the inclusion of metallic oxides. If, as an extreme case, it is assumed that all of this oxygen was present in the form of cuprous oxide, Cu_2O, and that none of this oxide was in solution but all of it was present as inclusions, conditions that are not at all likely to occur, the volume of such inclusions would still be less than 0.5 per cent of that of the sample. It is concluded, therefore, that the porosity prevailing in most dental castings is due largely to localized shrinkage or to occluded gas, or to both.

As noted above, porosity was especially noticeable in sections of the casting adjacent to the sprue. This porosity has the effect of weakening the castings in these sections to a very marked degree. It was found that this could be largely eliminated by the use of a very short sprue of large diameter, the shorter the sprue and the larger the diameter the better. Where the use of such a sprue is inconvenient, it was found that the same result could be accomplished by providing within the mold a chamber somewhat thicker than the thickest part of the pattern and as near as possible to the pattern without actually touching it. This is easily done by attaching a ball of wax to the sprue before applying the investing material. On casting this chamber is filled with molten metal which, because of its size, remains liquid until after the casting has solidified, thus serving as a reservoir from which additional molten metal is supplied to the casting as it shrinks during solidification. This method of spruing resulted in the production of castings which were as sound near the sprue as elsewhere. The method can be applied to many of the usual types of dental castings and should prove of value in reducing the porosity of these.

In order to determine as much as possible concerning the properties of dental castings, a large number of these castings were subjected to such tests as could be applied. These castings were divided into three groups according to the type of dental appliance they represented; namely, clasps, inlays, and saddles or partial dentures. The patterns for the clasps were made by bending a strip of No. 20 gauge (0.032 inch) wax, 1 inch long by $\frac{1}{8}$ inch wide around a cylinder $\frac{3}{8}$ inch in diameter. The inlays were slightly tapered cylinders approximately $\frac{1}{4}$ inch in diameter and $\frac{1}{8}$ inch thick. The saddles were sheets

1½ inches long, ½ inch wide, and No. 22 gauge (0.025 inch) thick with three round sections $\frac{3}{16}$ inch in diameter built up to $\frac{3}{32}$ inch in thickness. A number of each of these castings were made of each of five alloys selected from the so-called hard, medium, and soft groups. The methods of spruing, investing, and burning out of the molds were varied between wide limits. The temperature of the molds at the time of casting was varied from slightly above room temperature to about 650° C. (1,200° F.). Both air pressure and centrifugal casting machines were used.

The castings were given the desired heat treatment, sectioned, and tested for Brinell hardness. Microscopic examinations for internal porosity and characteristic structure were made also. Comparison of these data with corresponding data obtained from tensile specimens of various sizes and cast in various ways proved of great value in selecting a method of preparing satisfactory tensile specimens.

The values obtained for the Brinell hardness of these dental castings are summarized in Table 14. The different types of castings agreed very closely in hardness, the differences between types being no greater than those between duplicate samples of the same type. Since the micrographic data obtained are of value chiefly as a partial identification of the materials tested and as a further verification of the analogy between dental castings and the tensile samples used, these data also are presented and discussed at this time.

TABLE 14.—*Mechanical properties and melting ranges of cast-gold alloys*

Alloy	Heat treatment [1]	Tensile properties				Brinell hardness number		Melting range	
		Proportional limit	Ultimate strength	Elongation in 3 inches [2]	Modulus of elasticity [3]	Tensile specimens	Dental castings		
		Lbs./in.²	*Lbs./in.²*	*Per cent*	*Lbs./in.²*			*°C.*	*°F.*
24-carat		[4] 1,000	16,500	34		27		1,063	1,945
XXVI		17,500	48,000	31	11,000,000	76		925–940	1,700–1,725
XXVII		3,000	21,500	25		32		1,030–1,050	1,885–1,920
XXVIII		11,000	34,500	20		54	52	970–1,020	1,775–1,875
XXIX		11,000	36,000	19	11,000,000	56		925–995	1,700–1,825
XXX		18,000	45,500	18	12,000,000	74		895–980	1,650–1,795
II	Softened	22,500	48,000	18	11,000,000	90	82	940–1,025	1,725–1,875
	Hardened	26,500	50,500	14	12,000,000	98	94	940–1,025	1,725–1,875
I	Softened	50,000	64,500	1	13,000,000	154	150	910–1,010	1,665–1,850
	Hardened	61,000	84,000		13,000,000	195	196	910–1,010	1,665–1,850
V	Softened	46,000	70,000	10	13,000,000	149	148	820–870	1,510–1,600
	Hardened	73,000	103,000	1	13,000,000	214	202	820–870	1,510–1,600
IV	Softened	53,500	69,000	4	13,000,000	145	143	885–985	1,620–1,805
	Hardened	94,500	108,500		14,000,000	249	222	885–985	1,620–1,805
S–V		20,500	37,500	18	11,000,000	78		745–870	1,375–1,595
S–IV	Softened	24,000	36,000	7	11,000,000	103		755–835	1,390–1,535
	Hardened	61,500	70,000		12,000,000	180		755–835	1,390–1,535
S–III	Softened	30,000	44,000	9	12,000,000	111		765–800	1,410–1,470
	Hardened	77,000	92,000		13,000,000	199		765–800	1,410–1,470
S–II	Softened	29,500	44,500	12	11,000,000	103		750–805	1,385–1,480
	Hardened	77,500	83,500		12,000,000	193		750–805	1,385–1,480
S–I	Softened	27,000	42,500	14	11,000,000	111		745–785	1,375–1,445
	Hardened	55,000	63,000	1	12,000,000	185		745–785	1,375–1,445

[1] In this table the heat treatments designated by "softened" and "hardened" consist of quenching in water from 700 °C. and cooling slowly from 450 °C., respectively. Those alloys for which no heat treatment is indicated were not appreciably affected by these treatments.

[2] Where no value for elongation is given, the value obtained was less than 1 per cent.

[3] Where modulus of elasticity is not given, this value was not determined.

[4] Less than 1,000.

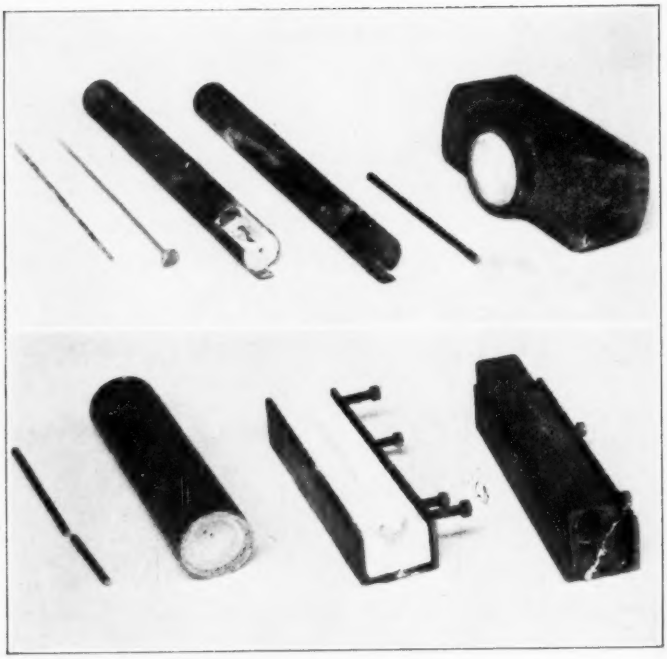

FIG. 26.—*Types of molds used for casting test specimens, and some of the castings produced*

With this preliminary work completed, the development of a method of preparing satisfactory tensile specimens was undertaken. It was desired to use a specimen as small as would be consistent with the required accuracy of test, both for the reason that it was thought that the properties of small castings would more nearly agree with those of dental castings and because of the fact that the cost of the relatively large samples commonly employed in testing engineering materials would, in many instances, make them impracticable.

With these considerations in mind, castings of various shapes and sizes were made by a variety of methods and compared with the dental castings of the corresponding alloys. Some of these castings were made with the usual dental laboratory equipment, including both air pressure and centrifugal casting machines, using methods commonly employed in dental practice. Others were made by melting the metal in a suitable crucible and casting or pouring it into well-vented investment or hard carbon molds. Both flat strips and round rods were cast. In some instances it was found desirable to use special flasks adapted to the size and shape of the castings being made. A number of the types of molds employed and some of the castings produced are shown in Figure 26.

Comparisons of these castings with dental castings of corresponding alloys indicated that satisfactory tensile specimens could be cast with an air pressure or centrifugal casting machine or by pouring into suitable molds. Either flat strips or cylindrical rods up to one-eighth inch in diameter could be produced, which agreed very closely with the corresponding dental castings in Brinell hardness and microstructure. In general, the thin castings were freer from internal porosity than those of larger cross section. The tensile properties of a number of samples produced by the different methods described were determined and found to be in very good agreement. The variations between samples produced by the different methods were no greater than those between duplicate samples produced by the same method.

The method of casting into well-vented carbon molds was finally selected as being the most satisfactory for this investigation. This method has the advantage that variables in the casting process are more readily controlled, thus insuring greater uniformity from sample to sample and a lower percentage of casting failures. Of the castings produced by this method only about 5 per cent were discarded because of defects. The use of carbon rather than investment molds has the advantage that the carbon is more durable and less likely to warp.

In conformity with the general principle, recognized by the American Society for Testing Materials and leading engineers, that tensile specimens of circular cross section yield more consistent and reliable results than those of rectangular section, the cylindrical rod type of specimen was adopted. The samples used for most of these tests

were approximately ⅛ inch in diameter and 5¾ inches long. Reference to the values for Brinell hardness given in Table 14 and to the micrographs of typical internal porosity and microstructure presented in Figures 27 to 31, inclusive, will show that the test specimens are very similar in these properties to the corresponding dental castings. When necessary, the rods were dressed down slightly with a fine file or emery paper to remove roughness or other minor irregularities of the surface. The diameter of individual rods was uniform from end to end to within approximately 0.002 inch.

The heat treatments given these alloys were similar to those developed for the wrought alloys and described in a previous section. After heat treatments were completed, a small section approximately ⅛ inch long was cut from each end of the rod. These small samples were mounted in a matrix of sulphur, ground and polished and tested for Brinell hardness. The same samples were also used for the microscopic examinations for internal porosity and microstructure.

Micrographs showing the types of internal porosity found and the characteristic microstructure of the alloys tested, together with corresponding micrographs of the dental castings previously described, are presented in Figures 27 to 33, inclusive. No marked difference between the structure of any of these alloys in the softened condition and in the hardened condition was observed. In most instances the structure of the alloy in only one condition is shown. In comparing the micrographs of internal porosity it should be borne in mind that these micrographs are representative of the characteristic types of porosity observed rather than of the average condition of the entire casting. Since these defects usually are not uniformly distributed throughout the casting, it is difficult to obtain micrographs showing average conditions.

The Brinell hardness determinations were made with the same instrument used in the investigation of the wrought alloys and shown in Figure 20. For cast alloys having a hardness number greater than 50 a load of 12.8 kg (28.2 pounds) was used.

After the small samples for hardness tests and microscopic examination were cut from the rod the rest of the casting was used for the tensile tests. Most of these tests were made with a universal testing machine of 2,000 pounds capacity, in which the load was applied through four screws and measured by means of a beam and counterpoise. This machine was equipped with a self-aligning device, clamps, and an extensometer, which were designed and built especially for this investigation. A few of the tests on the alloys of very low strength were made with a machine of the pendulum type, having a capacity of 600 pounds.

In order to use as short a specimen as possible, short lugs of suitable shape were attached to the ends of the test rod by means of gold

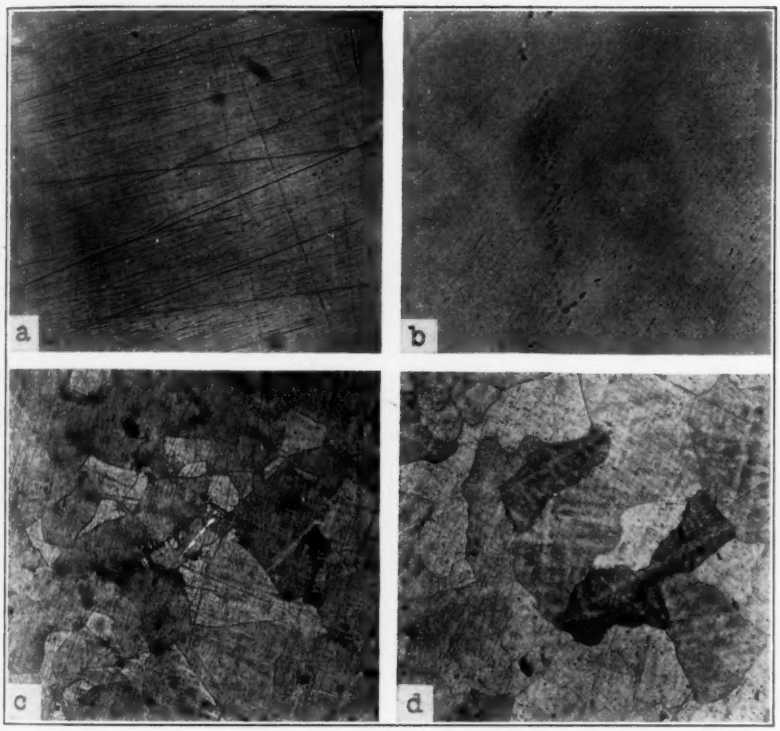

FIG. 27.—*Micrographs of Alloy XXVIII showing agreement in characteristic structure of different types of castings*

a, Porosity in dental casting, × 90; *b*, Porosity in test specimen, × 90; *c*, Microstructure of dental casting, etched with K C N, × 90; *d*, Microstructure of test specimen, etched with K C N, × 90.

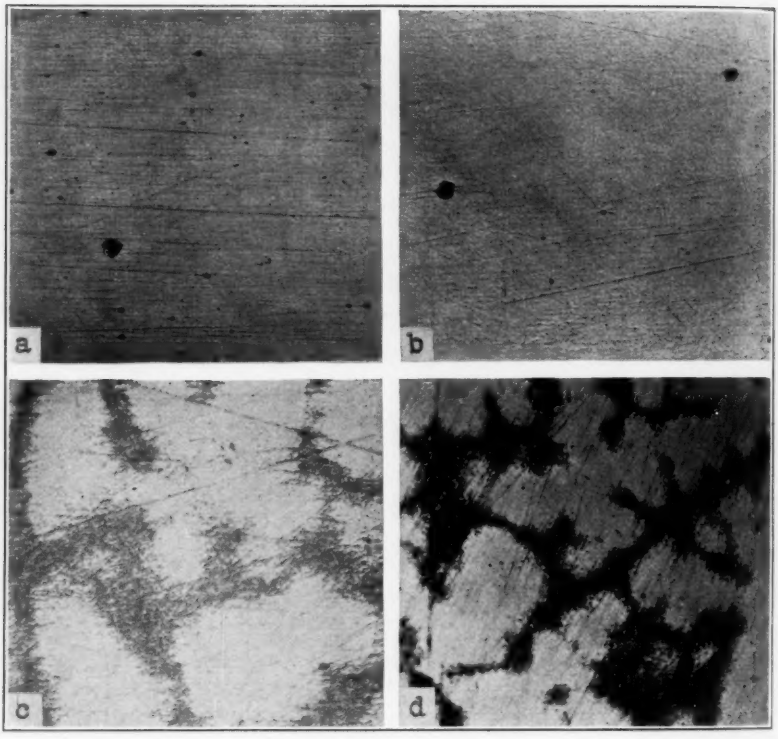

FIG. 28.—*Micrographs of Alloy II showing agreement in characteristic structure of different types of castings*

a, Porosity in dental castings, × 90; *b*, Porosity in test specimens, × 90; *c*, Microstructure of dental castings, etched with iodin, × 450; *d*, Microstructure of test specimens, etched with iodin, × 450.

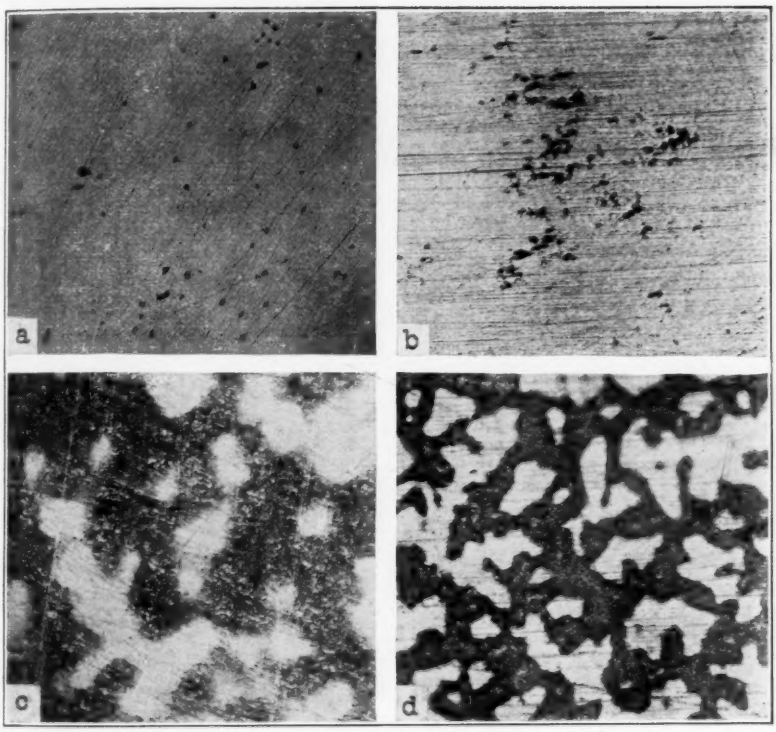

FIG. 29.—*Micrographs of Alloy I showing agreement in characteristic structure of different types of castings*

(*a*) Porosity in dental castings, × 90; *b*, Porosity in test specimens, × 90 (shows the center of a section near the sprue and is typical of shrinkage "pipes"); *c*, Microstructure of dental castings, etched with iodin, × 450; *d*, Microstructure of test specimens, etched with iodin, × 450.

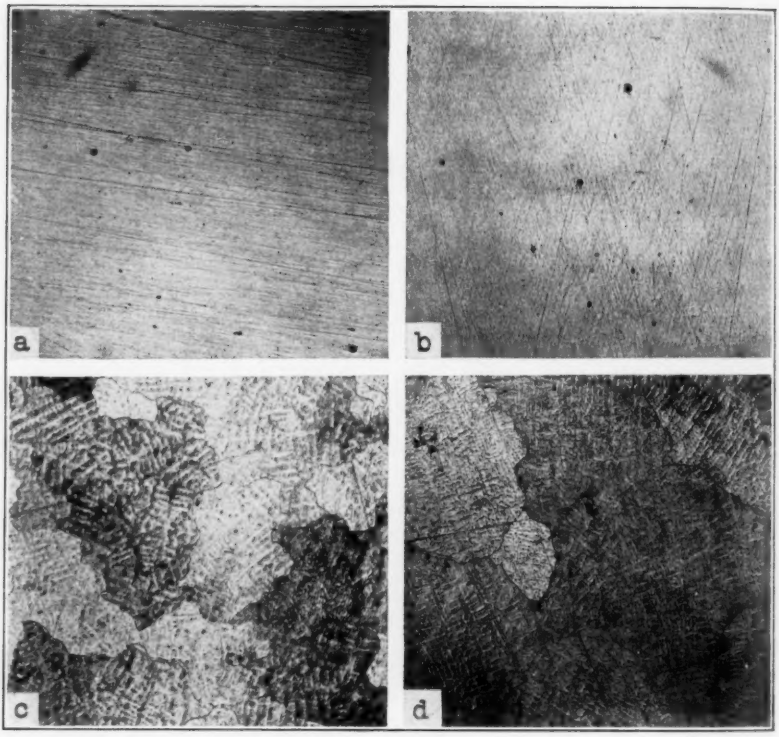

FIG. 30.—*Micrographs of Alloy V showing agreement in characteristic structure of different types of castings*

a, Porosity in dental castings, × 90; *b*, Porosity in test specimens, × 90; *c*, Microstructure of dental castings, etched with K C N, × 90; *d*, Microstructure of test specimens, etched with K C N, × 90.

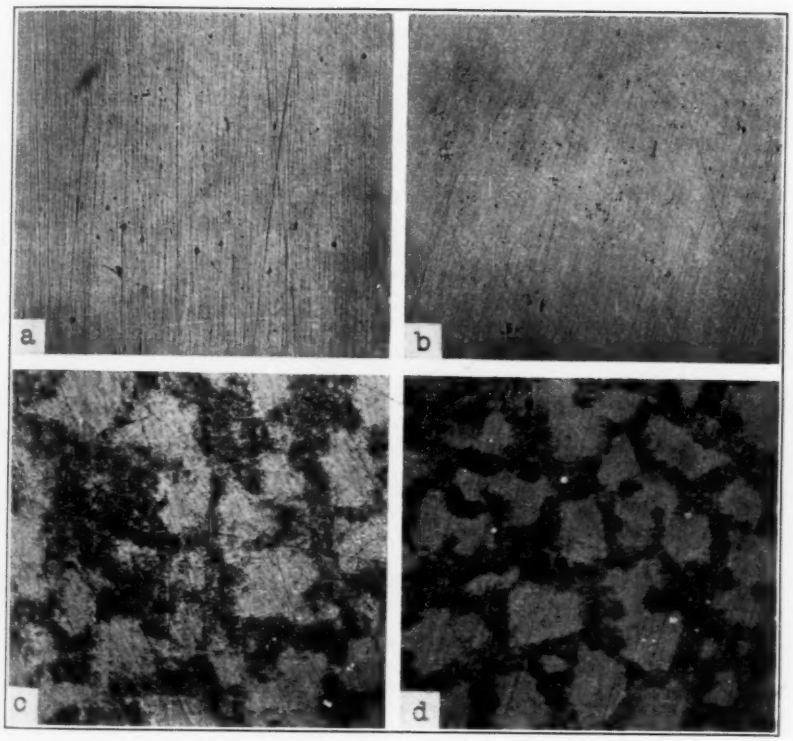

FIG. 31.—*Micrographs of Alloy IV showing agreement in characteristic structure of different types of castings*

a, Porosity in dental castings, × 90; *b*, Porosity in test specimens, × 90; *c*, Microstructure of dental castings, etched with iodin, × 450; *d*, Microstructure of test specimens, etched with iodin, × 450.

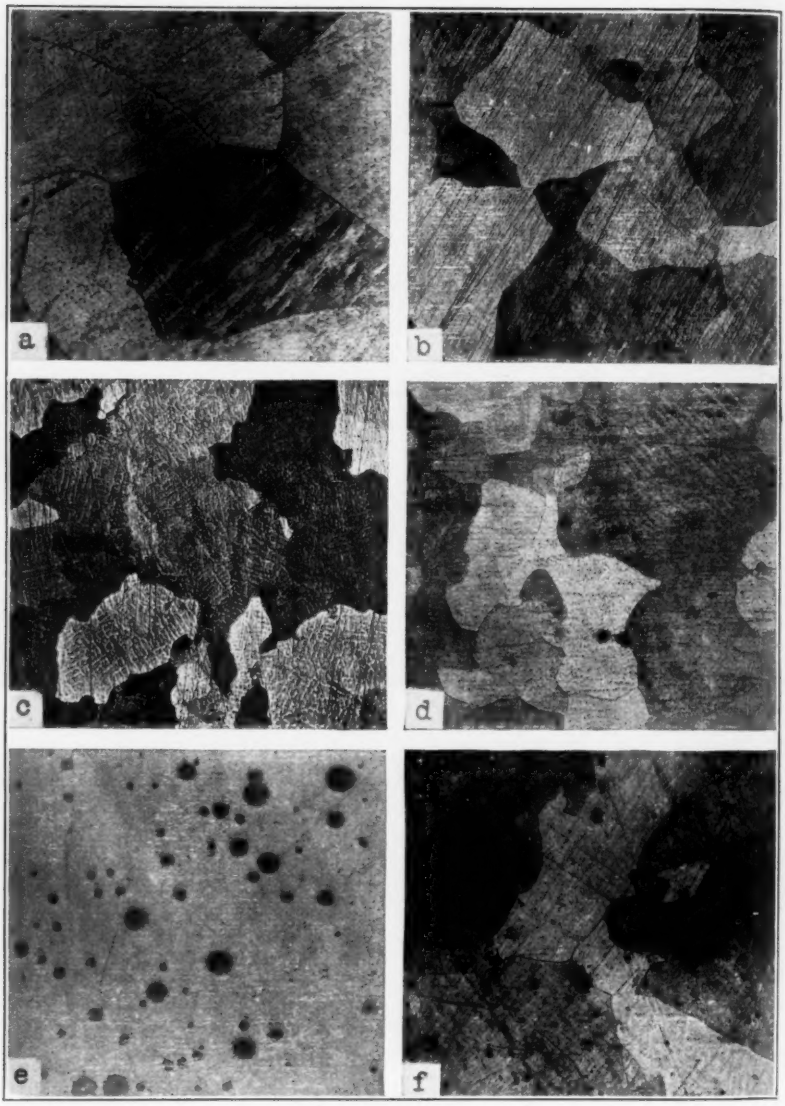

FIG. 32.—*Microstructure characteristic of five dental golds tested,* × 90

a, 24-k gold, etched with aqua regia; *b*, Alloy XXVII etched with iodin; *c*, Alloy XXIX etched with iodin; *d*, Alloy XXVIII etched with chlorin water; *e*, Alloy XXVI not etched, showing characteristic type of porosity, apparently due to occluded gas; *f*, Alloy XXVI etched with aqua regia.

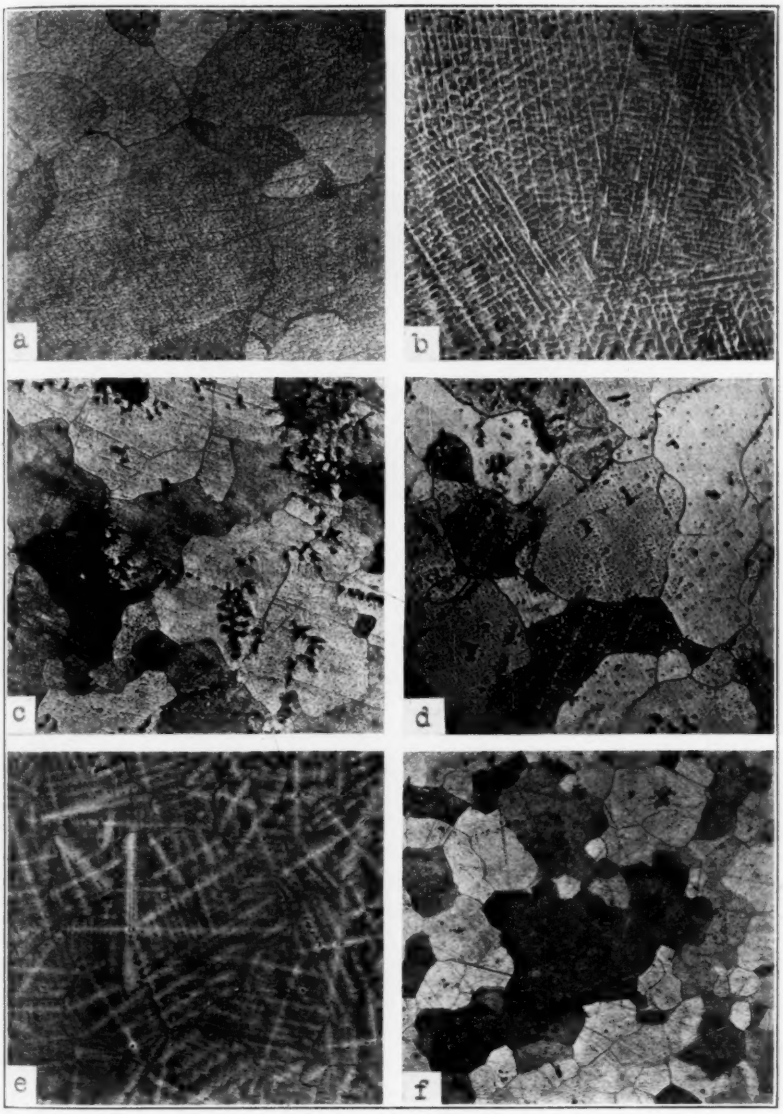

FIG. 33.—*Microstructure characteristic of the gold solders tested.* × *90*

a, Alloy S–I, etched with chlorin water and K C N; *b*, Alloy S–II etched with chlorin water and K C N; *c*, alloy S–IV, softened, etched with aqua regia; *d*, Alloy S–IV, hardened, etched with aqua regia; *e*, Alloy S–III etched with K C N; *f*, Alloy S–V etched with aqua regia. The dark dendritic patterns seen in *c*, are voids, probably caused by localized shrinkage.

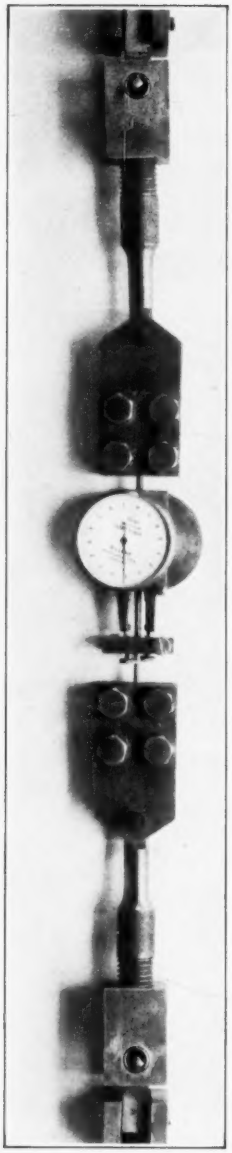

FIG. 34.—*Self-aligning device, clamps, and extensometer used in tensile tests of cast-gold alloys*

solder. These lugs were then held in the clamps of the testing machine. Although this method was very satisfactory for some of the alloys, it was found that specimens of other alloys, especially those melting at relatively low temperatures, would almost invariably fail near the solder. This was true even when a silver solder melting at a comparatively low temperature was used. While such tests might prove of value in a study of the effects of soldering, and certainly do indicate that the strength of some of these materials is lowered by the soldering process, they are not suitable for determining the mechanical properties of the individual alloys. This method was therefore abandoned and it was necessary to use longer samples. The clamps finally adopted, together with the self-aligning device and the extensometer, are illustrated in Figure 34.

The self-aligning device consists of an arrangement whereby each end of the specimen is mounted on a system of two knife-edges, one at right angles to the other. This arrangement compensates for possible misalignment of the head of the testing machine.

The extensometer is similar in principle to the one used and described in connection with the study of wrought alloys and consists essentially of two dial micrometers mounted on opposite sides of the specimen. The micrometers measure the extension of that portion of the specimen lying between the two points of attachment, commonly called the gauge length. The effective gauge length of this extensometer is 2.85 inches. The micrometers are graduated in 0.0001 inch, and the error does not exceed 0.00002 inch.

In carrying out these tests the extensions, or deformations, corresponding to small load increments were observed and recorded until a stress well above the proportional limit or until the ultimate strength of the specimen was reached. In every case the specimen was loaded to rupture and the maximum load recorded as the ultimate strength. The loads and the corresponding deformations were then plotted to form the usual stress-strain diagrams. Proportional limit and modulus of elasticity were determined from these diagrams except in the case of materials having very low proportional limits, for which moduli were not determined. Typical stress-strain diagrams for a number of these alloys are shown in Figure 35. The elongation, or the ratio of the increase in length caused by tensile stress, to the original gauge length was measured after rupture of the sample. The gauge length used was 3 inches.

Of the 35 alloys—the compositions of which are given in Table 10—14 were selected for complete tests. This list includes alloys intended for a variety of uses. In some instances, where alloys intended for the same use were markedly different in composition two or more were selected from the same group. The mechanical properties of 24-carat gold were determined also.

Determinations were made of the mechanical properties of at least three samples of each of these materials in each of the two conditions of heat treatment described. Where it was found that the different heat treatments produced no appreciable difference in the properties, only one series of values is reported. The values obtained for the various properties are presented in Table 14.

It is of interest to note that the relation between tensile strength and Brinell hardness, found to be nearly constant for the wrought alloys, is quite variable for the cast materials in this group. This is probably due to the fact that the castings are less homogeneous than the wrought alloys.

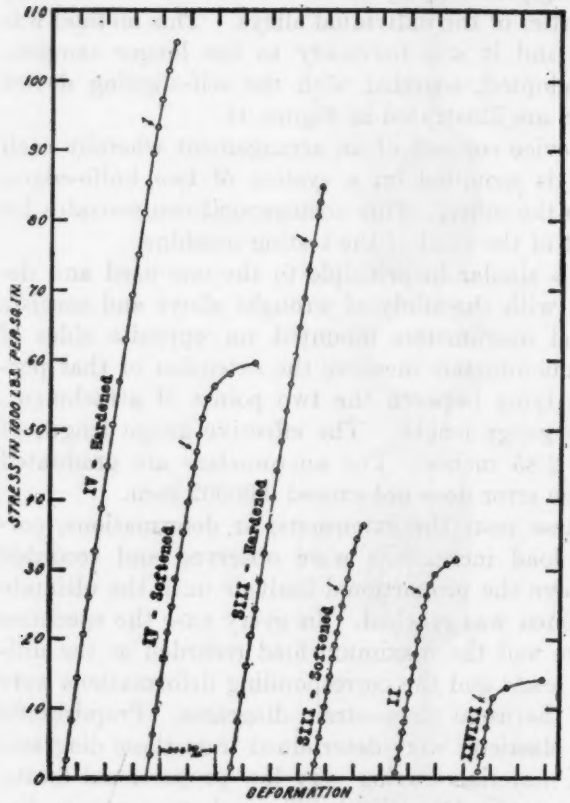

FIG. 35.—*Stress-strain curves derived from tensile tests of cast gold alloys*

Proportional limits are indicated by the arrows

An inspection of Table 14 will show wide variations in most of the properties determined. The values for proportional limit range from less than 1,000 to nearly 95,000 lbs./in.^{2}, and the Brinell hardness numbers from 27 to 249 for 24-carat gold and Alloy IV, respectively. The elongations range from less than 1 per cent for several of the alloys to 34 per cent for 24-carat gold. There are also marked differences in the melting ranges of the various alloys. Manifestly, there is a decided choice possible in selecting materials suitable for any specific purpose and definite values for the properties reported in this table are necessary for making the most efficient selection.

The following data on a few gold-foil fillings are included in this section for comparison with the cast-gold inlay. In securing these data six members of the dental profession, including recognized

leaders in this field, were asked to cooperate in preparing test fillings. These cooperators were supplied with split steel molds or cavities one-eight inch square by three-sixteenths inch deep and with a quantity of gold foil, with the request that they fill the cavities, using as nearly as possible the technique employed by them in practice. The foil used was one of the well-known brands supplied to the profession, the same brand and grade being used throughout the tests. The fillings prepared by the cooperators were tested for density and Brinell hardness. They were also examined under the microscope for characteristic structure.

In determining the densities reported the volume of the test filling was calculated from micrometer measurements of its linear dimensions. The density was obtained by dividing the weight of the filling by this volume. For practical purposes the value for density obtained by this method may be considered as the weight of foil condensed into the cavity per unit volume of cavity. If there are irregularities in the surfaces of the fillings, due to imperfect adaptation to the cavity walls, this value was found to be slightly lower than that obtained by the usual method of weighing the sample in two media of different densities, such as air and water. Although density was determined by both methods, it is thought that in this instance the values obtained by the latter method are not so significant as those reported.

The fillings were sectioned, some perpendicularly to the direction of packing and others parallel to the direction of packing. Brinell hardness determinations were made at several points on each of these sections using the instrument previously described with a load of 6.4 kg (14.1 pounds). The values obtained for the density and Brinell hardness of the six fillings tested are given in Table 15. The Brinell hardness of three soft cast-inlay golds are also included in the table for ready comparison. Micrographs showing characteristic structure are presented in Figure 36.

TABLE 15.—*Properties of foil fillings and soft inlay golds*

Foil fillings			Cast-inlay golds	
Sample No.	Density	Brinell hardness number	Material	Brinell hardness number
	g/cm [3]			
1	17.0	[1] 36	24-carat gold [3]	27
2	17.3	50		
3	14.2	[2] 18	Alloy XXVII; 22-carat gold (0.5 per cent copper)	32
4	16.8	51		
5	18.2	61	Alloy XXVIII; 22-carat gold (3.7 per cent copper)	54
6	19.0	60		
Average	17.1	46		

[1] Brinell hardness of different spots varied from 22 to 46.
[2] Brinell hardness of different spots varied from 13 to 26.
[3] Density of 24-carat cast gold is 19.3 g/cm [3] (Smithsonian Physical Tables, 7th ed., p. 110).

By referring to Table 15 it will be noted that there are marked variations in the properties of the different fillings. The densities range from 14.2 g per cubic centimeter for sample No. 3 to 19.0 g per cubic centimeter for sample No. 6, and the Brinell hardness numbers from 18 for sample No. 3 to 61 for sample No. 5. It will also be noted that samples Nos. 1 and 3 are quite variable in hardness from place to place. The remaining samples were much more uniform.

The values obtained by averaging the six samples tested are 17.1 g. per cubic centimeter for density and 46 for Brinell hardness number. Using these values as a basis of comparison, it is seen that the gold-foil filling is markedly harder than an inlay cast of 24-carat gold. It is nearly as hard as an inlay cast of a 22-carat gold containing 3.7 per cent copper. The density is less than that of cast 24-carat gold.

(d) CASTING SHRINKAGE

The casting shrinkage of gold may be divided into three parts; namely, (1) the contraction of the liquid metal on cooling from the temperature at which it enters the mold to the freezing point, (2) the contraction of the metal on changing from the liquid to the solid state at constant temperature (1,063° C., 1,945° F. for pure gold), and (3) the contraction of the solid gold on cooling from the freezing point to room temperature.

A search of the literature failed to reveal any reliable value for part (1). Price,[15] in his classical experiment, using a fused quartz mold, determined values for parts (2) and (3). These values he reported to be 1.46 per cent linear contraction due to change of state without change of temperature and 2.20 per cent linear contraction from the freezing point, 1,063° C. (1,945° F.) to 0° C. (32° F.). Price concludes that under favorable conditions all of the contraction of the gold, except that which occurs after the metal has solidified, is compensated for by the addition of liquid gold from the crucible.

It was thought advisable to verify this conclusion and determine the net casting shrinkage (or that which affects the dimensions of the casting) for some of the alloys of gold. The thermal contraction of the metal in the solid state was determined for 24-carat gold and some of its binary alloys. The apparatus [16] used in making these determinations was that regularly used at this bureau for determining the thermal expansion of solids. A photograph of the instruments with a brief description is presented in Figure 37. The samples used were rods 30 cm long and approximately 1 cm in diameter. The temperature range for these tests was from the maximum temperature at which the sample was sufficiently rigid to maintain its shape without sagging, to room temperature. From the values determined in this

[15] Price, W. A. Dental Cosmos, p. 265; March, 1911.

[16] For a detailed description of this apparatus see Souder and Hidnert, B. S. Sci. Paper No. 524, 21, p. 1; 1926.

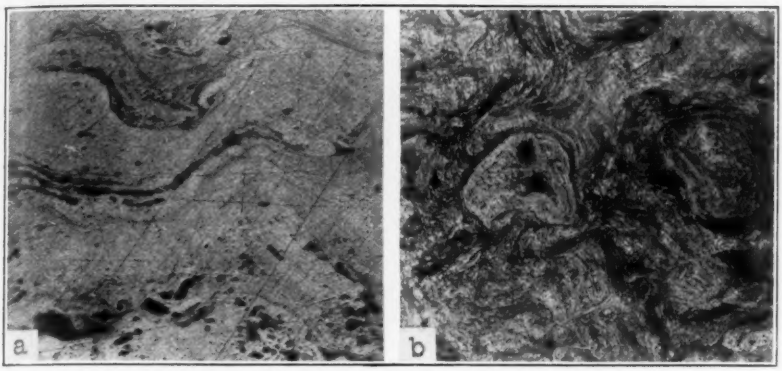

FIG. 36.—*Micrographs of gold-foil fillings, etched with aqua regia,* × *90*

a, Section parallel to the direction of packing; *b*, section perpendicular to the direction of packing. Note the laminated structure and voids due to incomplete condensation.

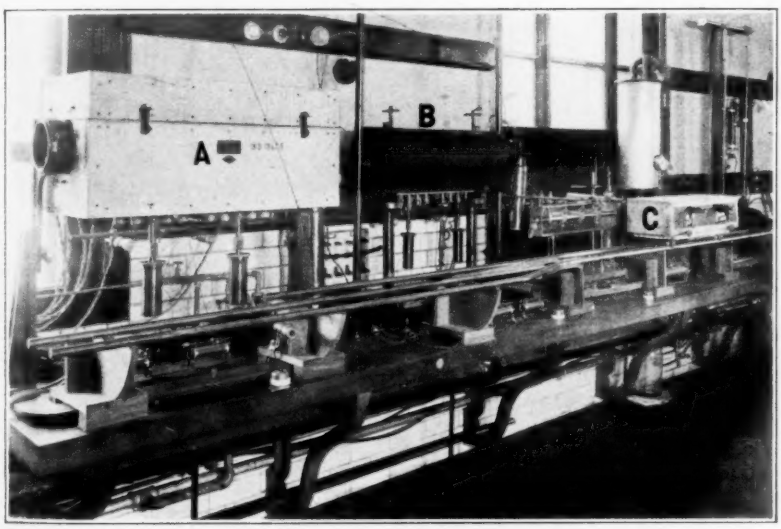

FIG. 37.—*Apparatus for determining the thermal expansion of solids*

Electric furnaces for heating the samples are shown at *A* and *B*. The sample is placed in the furnace in a horizontal position and may be supported throughout its length. Very fine wires are passed over the ends of the sample and allowed to hang down through the tubes in the bottom of the furnace and are viewed through slots in the tube. Length changes, which are transmitted to the wires, are measured with micrometer microscopes mounted on a movable carriage shown at *C*. The furnace temperature is measured with thermocouples and a potentiometer.

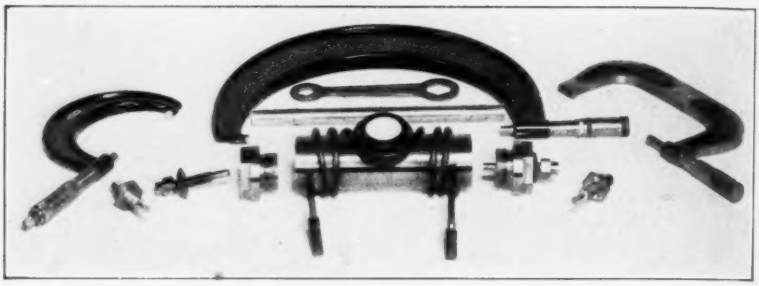

FIG. 38.—*Apparatus for determining the net casting shrinkage of golds*

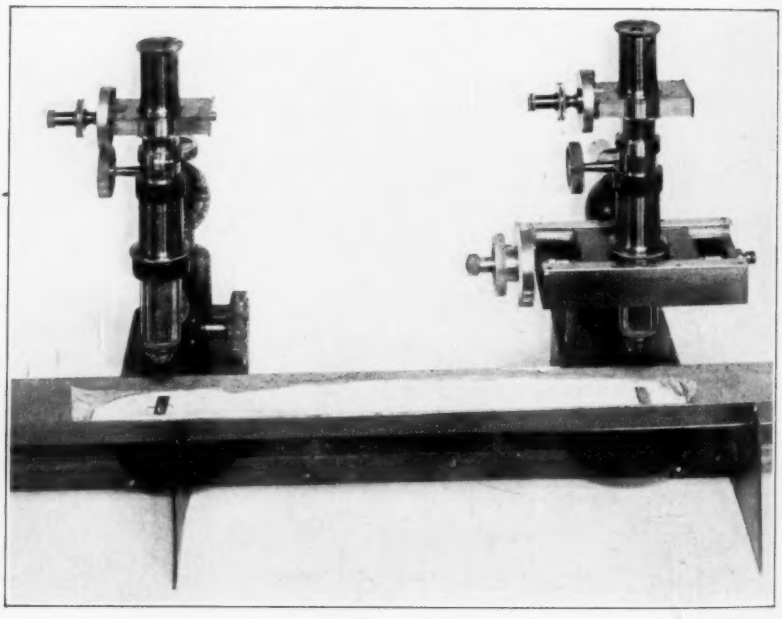

FIG. 45.—*Apparatus for measuring setting changes of investments*

manner the total contraction from the melting point to room temperature was calculated by extrapolation. The values are given in Table 16. The apparatus used for measuring the net casting shrinkage is shown in Figure 38. The test procedure was as follows: The large caps were screwed tightly into the ends of the flask and the small hollow plugs screwed into the caps and locked in position with lock nuts. A metal rod, inserted through and supported by the hollow plugs, served as the pattern. The sprue was attached to the pattern with wax, the crucible former placed in position and the flask filled with investment. After the investment had set the crucible former, sprue, and pattern rod were removed. The hollow plugs were replaced with the solid plugs, thus forming a mold, the length of which is determined solely by the distance between the inside faces of the solid plugs. The flask was then placed in an oven and "burned out" at the desired temperature. The casting was made with an air-pressure machine in the ordinary manner.

TABLE 16.—*Thermal contraction of golds*

Material	Maximum temperature of test	Observed contraction from maximum temperature to 25° C.	Melting point [1]	Computed contraction from melting point to 25° C.
	° *C.*	*Per cent*	° *C.*	*Per cent*
24 carat	1,044	1.71	1,063	1.76
90 Au, 10 Ag	973	1.79	1,046	2.03
90 Au, 10 Cu	860	1.48	926	1.62
90 Au, 10 Ni	886	1.55	935	1.91

[1] In this table, "melting point" is used to designate that temperature at which solidification is completed.

The metal parts of the apparatus are of an oxidation-resisting steel, the coefficient of thermal expansion of which is known. The temperatures of various parts of the flask were measured with small thermocouples and a potentiometer. The length, at room temperature, of each of the solid plugs was accurately determined. The distance between the outside faces of the solid plugs was measured with a micrometer. From these values the distance between the inside faces of the solid plugs, or the length of the mold, was computed.

After the casting had cooled to room temperature it was removed from the mold and its length measured with a micrometer. The difference between the length of the casting and the length of the mold is the net shrinkage of the casting. The castings were approximately 3¼ inches long and 0.12 inch in diameter.

The temperature of the molds in which the castings were made was varied from approximately 300° C. (570° F.) to slightly above room temperature. The temperature of the metal was varied from the lowest at which a casting could be made to the maximum temper-

ature obtainable with a good blowpipe, using hydrogen and compressed air. The casting pressure was varied from 5 to 20 lbs./in.^{2}

A complete series of tests were made for one alloy, alloy XXVI (90 Au, 10 Cu). The values obtained are given in Table 17. A few tests by this method on other alloys and rougher measurements of the shrinkage of a large number of castings made for tensile test specimens indicated that no large variations from these values, due to variations in composition of the alloy, are to be expected for gold alloys within the range of composition commonly employed in dentistry.

It will be noted that the variations in the casting conditions had little, if any, effect, and that in every case the effective shrinkage is less than that of the solid metal from the melting point to room temperature. The average of the values for net casting shrinkage given in Table 17 is 1.25 per cent, whereas the contraction of the solid metal is 1.62 per cent.

TABLE 17.—*Casting shrinkage of a gold-copper alloy (90 au, 10 cu)*

Temperature of mold (approximate)	Casting temperature of gold	Casting pressure	Net casting shrinkage
		Lbs./in.^{2}	*Per cent*
40° C	Moderate	20	1.2
40° C	do	10	1.2
300° C	do	10	1.2
300° C	High	10	1.2

Two possible explanations of this difference are suggested: (1) There may be sufficient friction or interlocking between the casting and the walls of the mold to hold and stretch the casting while it is cooling through that range of temperature within which the metal is very soft or weak, thus preventing the full normal shrinkage, and (2) the compensation of part of the total shrinkage of the solid metal may be dependent upon a difference in the rates of cooling of different parts of the casting. If part of the metal in the mold solidifies and cools to some temperature below the melting point before the metal in the sprue freezes, the shrinkage due to the cooling of this solid metal may be compensated by the addition of metal from the crucible.

The shrinkage of the liquid metal before the sprue freezes obviously would be compensated by the addition of metal from the crucible if the casting pressure were maintained. If a crust of solid metal has formed around the entire outside surface of the casting before the central part of the casting freezes, the shrinkage of this central portion as it cools to the freezing point may produce voids or porosity previously referred to as localized shrinkage in the casting. Such localized shrinkage would not affect the outside dimensions of the casting.

In the case of shorter, bulkier castings the stretching force of the mold might not have so great an effect. The addition of more metal from the crucible would be less effective because of the relatively faster rate of freezing of the metal in the sprue. The shrinkage of such castings would probably be slightly greater than the values reported.

The effect of the casting temperature on the shrinkage of an alloy of 95 per cent aluminum and 5 per cent copper was determined in a different manner on larger castings. Molds were made of molding sand by ordinary foundry methods, using a pattern approximately 35 cm long by 1 cm square. Small steel plates were placed at each end of the mold to provide smooth end surfaces against which to cast. The distance between the end plates was measured with a scale divided to 0.5 mm. The metal was melted according to regular foundry practice, except that the temperature was carried much higher than usual. The temperature of the metal in the ladle was measured with a thermocouple. Some of the molds were poured with metal at 1,030° C. (1,885° F.) and the remaining molds were poured when the metal had cooled to 725° C. (1,335° F.). After cooling the length of the castings was measured.

The average shrinkage of the castings poured at 1,030° C. (1,885° F.) was 1.61 per cent and of those poured at 725° C. (1,335° F.) 1.64 per cent. This indicates that the casting temperature has very little effect on the shrinkage and serves as a check on the method described above.

3. SELECTION OF DENTAL GOLD ALLOYS

In the foregoing sections various properties of dental gold alloys have been defined, and the significance of these properties in relation to the behavior of the alloys in service has been pointed out. From the data presented it is evident that the selection of a suitable alloy for a given use can be made on the basis of these physical properties. The principles of such a method of selection are embodied in the tentative specifications [17] for dental gold alloys now being used in purchasing these materials for use by the various Government departments. These specifications were formulated by the Bureau of Standards in cooperation with the other Government departments concerned. In them definite minimum or maximum values are specified for such properties as proportional limit, tensile strength, percentage elongation, Brinell hardness, fusion temperature, and others. The values specified are based upon a combination of the results of an investigation of the properties of the available materials and of a theoretical consideration of the properties required to meet the demands of service. As the values for the various properties required

[17] Souder, Wilmer, "Summary of reports on dental alloys"; J. A. D. A.; April, 1928.

in the present specifications are tentative and are being revised as improvements are suggested, they are not included here. The principles of this method of selecting dental gold alloys, as outlined, are sufficient to illustrate a practical application of the data developed in this investigation. The perfection and general adoption of such a method would undoubtedly eliminate much of the waste incident to the use of unsatisfactory materials.

III. ACCESSORY MATERIALS USED IN THE DENTAL CASTING PROCESS

In order to determine the possible causes of dimensional inaccuracies of cast gold appliances other than the inaccuracies due to the casting shrinkage of the gold alloys, an investigation was made of the properties of the waxes used for making the pattern and the investments used for making the molds for these castings. It was thought that such an investigation might result in the development of methods of manipulating these materials that would not only avoid the introduction of further inaccuracies, but also compensate for the shrinkage of the cast gold alloys.

1. PATTERN WAXES

In the usual dental casting process the pattern for the casting is made by building up the appliance in pattern wax. The wax is warmed to a temperature at which it becomes soft and plastic, usually 40 to 50° C. (104 to 122° F.), depending upon its composition, and is adapted to the tooth or model in that condition. In order to determine the dimensional changes caused by the cooling of the pattern after being adapted, thermal expansion tests were made on five inlay pattern waxes. Four of these waxes, Nos. 1, 2, 3, and 4, were purchased on the open market and are believed to be representative of those in general use. Wax No. 5 was made up as an experimental material and contains 25 per cent carnauba, 60 per cent paraffin (55° C. melting point), 10 per cent ceresin, and 5 per cent refined beeswax with a very small amount of oil soluble coloring matter. This wax at ordinary room temperature is sufficiently hard to withstand the necessary handling without being distorted and can be carved without chipping or flaking. It becomes soft and plastic at temperatures between 45 and 50° C. (113 to 122° F.), and can be almost completely eliminated from the investment mold by heating to 250° C. (480° F.) or higher temperatures. This material was used in making many of the experimental castings. The apparatus used in making the thermal-expansion tests was that previously described and illustrated in Figure 37. The samples used were approximately 300 mm long and 5 mm in diameter. The length changes due to changes in temperature are represented graphically in Figures 39 to 43

and are summarized in Table 18. Values for the thermal expansion of an impression compound, used for taking impressions of the teeth and other parts of the mouth, are also included in the table and are represented graphically in Figure 44.

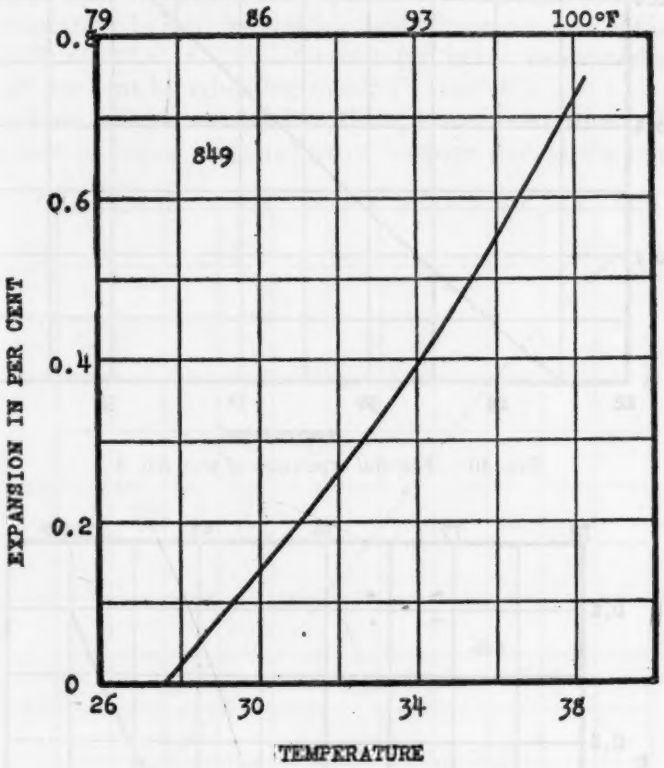

FIG. 39.—*Thermal expansion of wax No. 1*

TABLE 18.—*Thermal expansion of five inlay waxes and one impression compound*

Temperature range (in °C.)	Expansion (per cent)						Temperature range
	Wax No. 1	Wax No. 2	Wax No. 3	Wax No. 4	Wax No. 5	Impression compound No. 1	
							°F.
25 to 30	[1] 0.12	0.22	0.16	0.23	[1] 0.13	0.09	77–86
30 to 35	.32	.25	.30	.31	.34	.16	86–95
35 to 40	[2] .26	.24	[2] .29	.29	.25	.15	95–104
25 to 40	[3] .70	.71	[4] .75	.83	[5] .72	.40	77–104

[1] Temperature range 28 to 30° C.
[2] Temperature range 35 to 38° C.
[3] Temperature range 28 to 38° C.
[4] Temperature range 25 to 38° C.
[5] Temperature range 28 to 40° C.

By referring to the values given in Table 18 it will be seen that if a pattern made of any of these inlay waxes is made to fit the cavity or

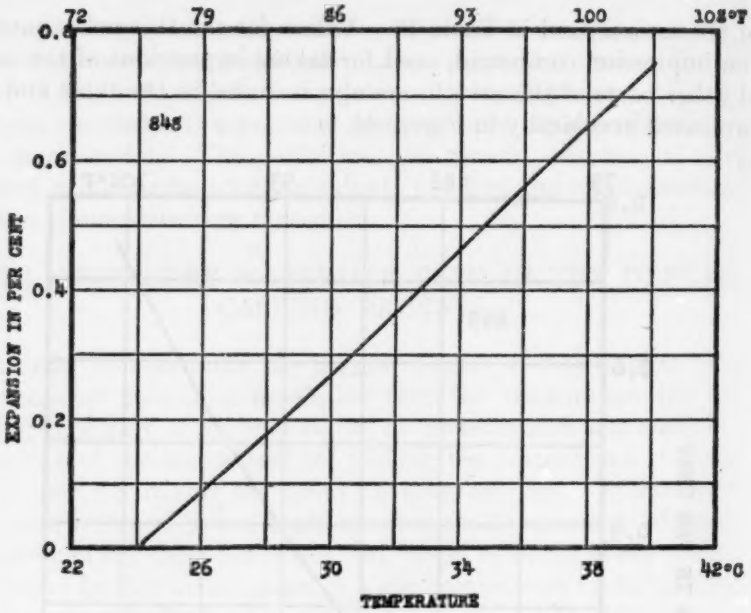

FIG. 40.—*Thermal expansion of wax No. 2*

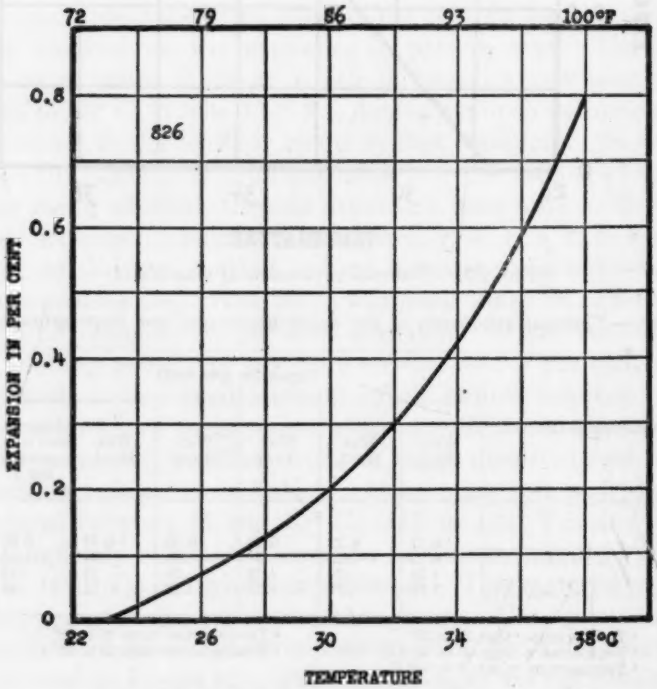

FIG. 41.—*Thermal expansion of wax No. 3*

model at 40° C. (104° F.) and allowed to cool to 25° C. (77° F.), the pattern will be too small by about 0.7 to 0.8 per cent, depending upon the wax used. These values also indicate the degree to which the shrinkage of the cast gold alloys may be compensated for by expanding the wax pattern as suggested by Dr. C. S. Van Horn [18] in 1910. If the wax pattern is held in position under pressure and chilled and made to fit at 25° C. (77° F.) for example, it can be expanded from 0.7 to 0.8 per cent by reheating to 40° C. (104° F.).

It has been pointed out by Van Horn, Price,[19] and others that if a wax pattern is heated a distortion or warpage due to the release of

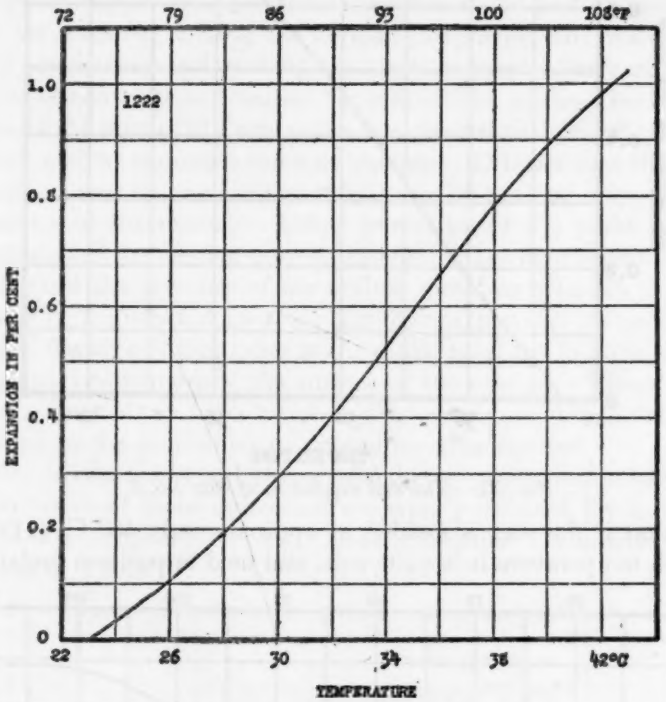

FIG. 42—*Thermal expansion of wax No. 4*

internal stresses is likely to result. Tests were made to verify this, and it was found that under certain conditions very serious distortions took place, but that by properly controlling conditions the effect could be so reduced as to be of no practical importance. These tests indicated that, in general, the softer a wax is when worked or the higher the temperature at which it is worked the higher will be the temperature to which it may be reheated without seriously distorting.

[18] Van Horn, C. S., "Castings; a review and commentary, including a technique"; Dental Cosmos, p. 873; August, 1910.

[19] Price, Weston A., "The laws determining the behavior of gold in fusing and casting"; Dental Cosmos, p. 265; March, 1911.

The length of time the wax is held at a given temperature on reheating also affects the amount of distortion. In general, the longer the time the greater the distortion will be. In the case of wax No. 5 it was

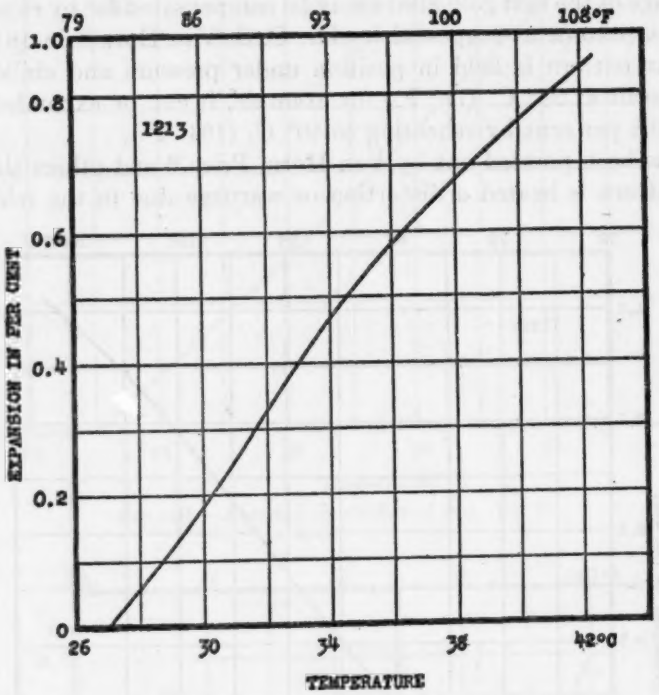

FIG. 43.—*Thermal expansion of wax No. 5*

found that if the wax is molded at approximately 48° C. (118° F.), at which temperature it is quite soft, and held in position under pres-

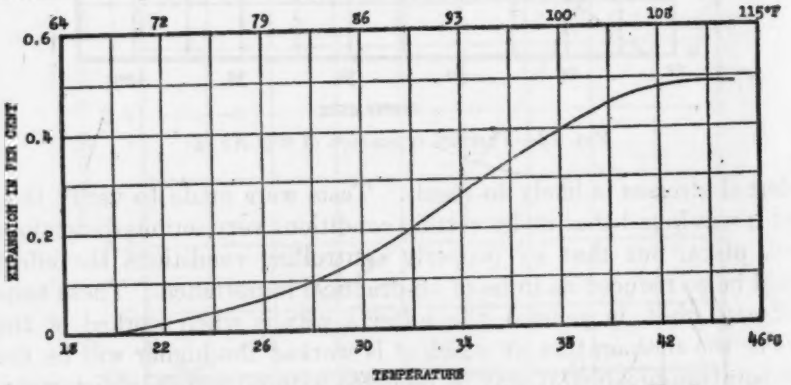

FIG. 44.—*Thermal expansion of impression compound No. 1*

sure while it is being chilled it may be reheated to 40° C. (104° F.) and held at that temperature for 45 minutes or longer without appreciable distortion.

By holding the pattern in position under pressure and chilling and, when necessary, adding small quantities of wax where required the pattern may be made to fit at 27° C. (81° F.) or even lower temperatures. If the pattern is made of wax No. 5, heating it from 27° C. (81° F.) to 40° C. (104° F.) will result in an expansion of 0.76 per cent, which can be used to compensate for part of the shrinkage of the cast gold alloy.

2. INVESTMENTS

Most of the investments or materials used for making the molds for dental castings consist chiefly of plaster of Paris and silica, although small quantities of other materials are often added as modifiers. The molds are made by mixing the investment powder and water to the desired consistency and pouring the mixture around the wax pattern. The investment sets or hardens because of the reaction between the water and the plaster of Paris and is then heated to drive off the excess moisture and to eliminate the wax pattern. Dimensional changes of the mold caused by the setting reaction or by heating may affect the dimensions of the casting. Other properties of the mold to which inaccuracies of the casting may be attributed are insufficient strength to withstand the pressure of the molten metal as it enters the mold, resulting in a distorted casting; insufficient porosity to permit the escape of the air or other gases in the mold, resulting in an incomplete casting; and roughness of the surface of the casting. These properties were determined for a number of investments and the effects of variations in the manipulative procedure were studied.

Eleven investments and two artificial stone compounds selected as representative of those in general use were purchased for test. The approximate composition of these as determined by chemical analysis [20] are given in Table 19.

TABLE 19.—*Approximate composition of investments and artificial stone compounds*

	Percentage by weight										
	No. 3	No. 5	No. 6	No. 7	No. 9	No. 10	No. 11	No. 13	No. 14	No. 18	No. 19
Calcined gypsum ($CaSO_4\frac{1}{2}H_2O$)	56	37	31	30	27	24	19	19	24	26	39
Anhydrite ($CaSO_4$)								77	74		
Siliceous matter (mainly silica)	41	59	67	68	72	73	80	2		72	58
Carbon (mainly graphite)		3									
Boric acid										1	2
Coloring matter and impurities	3	1	2	2	1	3	1	2	2	1	1

A number of experimental investments were made up and tested to determine the effects of the fineness of the silica, of varying the proportions of plaster of Paris and silica, and of the addition of small quantities of other materials.

[20] The author is indebted to T. P. Sager and R. B. Rudy, of the Bureau of Standards, for analyzing these materials.

(a) DIMENSIONAL CHANGES CAUSED BY SETTING

A photograph of the instrument used for determining the dimensional changes of investments owing to crystallization or setting is shown in Figure 45. The instrument consists of a V-shaped support for the investment and two micrometer microscopes attached to a common base. The investment is mixed and poured into the V-shaped support which is lined with waxed paper to prevent the investment from adhering to its walls. Two small metal plates, on which are ruled reference lines, are placed in position, one at each end of the sample. These plates are provided with short projections which are embedded in the investment and prevent motion of the plates relative to the sample. Any length change of the sample results in a corresponding change in the distance between the reference lines and is measured with the micrometer microscope. The length of the samples used was 30 cm, and the length changes were determined with an accuracy of 0.005 per cent of the total length. In some cases the increase in temperature, due to the setting reaction, was measured by means of a mercurial thermometer placed on the sample and covered with cotton wool. The values obtained are given in Table 20.

TABLE 20.—*Setting changes of investments*

Material		Ratio water to powder by weight	Maximum increase in temperature[1]	Length change in first 30 minutes	Maximum length change		Length change at end of 24 hours
No.	Plaster				Per cent	Age of sample in minutes	
	Per cent		*°C.*	*Per cent*			
1	100	0.67	15	+0.32	+0.32	18	+0.32
2		.43	5	+.13	+.15	1,440	+.15
3	56	.51	8	+.46	+.49	113	+.42
4	40	.46	6	+.02	+.02	12	+.00
5	37	.46		+.01	+.02	1,440	+.02
6	31	.33	5	+.01	+.01	19	−.00
7	30	.46	5	+.24	+.27	60	+.25
7	30	.57	4	+.21	+.22	84	+.14
7	30	.69	4	+.16	+.17	45	+.11
8		.50	2	−.05	−.17	1,440	−.17
9	27	.32	3	+.24	+.36	1,440	+.36
10	24	.40	4	+.18	+.24	1,080	+.24
11	19	.60	2	−.13	−1.85	1,380	−1.85
12	10	.46	0	−.00	+.01	1,471	+.01
12	10	.36	0	−.00	−.00	59	−.00
13[2]		.33			+.06	1,440	+.06
13[2]		.28			+.10	1,440	+.10
18	26	.40		+.11	+.21	1,440	+.21
19	39	.40		+.09	+.26	1,440	+.26
19	39	.27		+.02	+.46	1,440	+.46

[1] As measured with a thermometer on the surface of the sample. Temperature inside the sample was probably very slightly higher.
[2] Artificial stone compound.

It will be noted that most of the materials tested expanded on setting, the amounts of expansion ranging up to 0.5 per cent. In general, the expansion increases as the plaster content increases,

though this is not always true. Increasing the proportion of water decreases the expansion in most cases. It will be noted that investment No. 11 contracted 1.85 per cent on setting. This may be due in part to the high water ratio necessary because of the extreme fineness of the powder and in part to the low plaster content. The expansion of the two artificial stone compounds is seen to be comparatively small.

The rise in temperature on setting varied from 0° to 15° C. For the usual casting investment the rise in temperature is about 5° C. While this is sufficient to cause an appreciable expansion of the wax pattern, this effect was not observed in practice. This may be due to the fact that the evolution of heat occurs simultaneously with the setting of the investment, and that the expansion of the investment during setting is very nearly equal to that of the wax caused by the increase in temperature.

(b) DIMENSIONAL CHANGES CAUSED BY HEATING

The samples used for determining the dimensional changes of investments caused by changes in temperature were 30 cm long and similar to those used for determining setting changes. The apparatus used was the same as that shown in Figure 37. In some cases an additional thermocouple was embedded in the sample in order to determine the lag of the temperature of the sample behind that of the furnace. It was found that in these tests when the furnace temperature was increased the temperature of the center of the sample lagged appreciably until the free water was driven off and then rapidly approached that of the furnace, after which the two temperatures changed at practically the same rate. The slower the rate of heating the more nearly the temperature of the furnace represented that of the sample. The rate of heating employed in these tests was such that for the purposes of this report the temperature of the furnace may be taken as that of the sample, and the furnace temperatures are reported.

The dimensional changes caused by heating and by subsequent cooling are represented graphically in Figures 46 to 62 and are summarized in Table 21. From these it will be noted that most of the investments tested expand from room temperature up to a temperature of approximately 125° to 150° C. (255° to 300° F.). (If the rate of heating were slower, this temperature would be slightly lower.) At this temperature the free water is eliminated very rapidly, and part of the water of crystallization is driven off. This loss of water of crystallization is accompanied by a shrinkage, the magnitude of which is largely dependent on the percentage of plaster present. In the case of investment No. 1, 100 per cent plaster (fig. 46), this shrinkage is very large and continues as the temperature is raised to 560° C. (1,040° F.) (the maximum temperature reached in this test).

In the case of the investments containing 10 to 60 per cent plaster this first shrinkage is relatively small and takes place over a short temperature range. So far as the dimensions of the mold are concerned, it is of little importance. As the temperature is increased a second expansion takes place up to a temperature of 250° to 350° C. (480° to 660° F.), when a second shrinkage begins. In most cases this second shrinkage is much greater than the first and takes place over

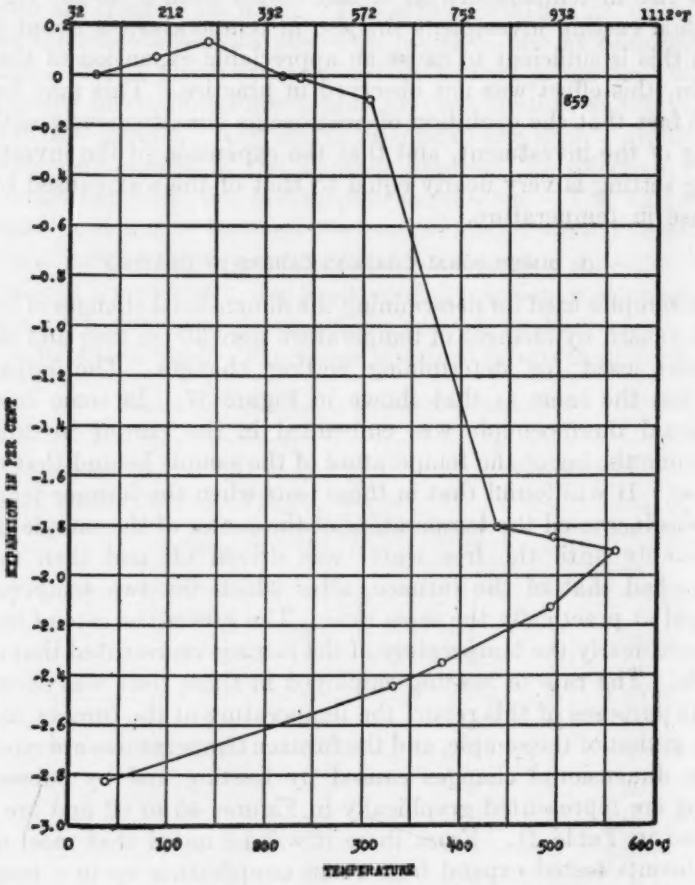

FIG. 46.—*Thermal expansion of investment No. 1*

a much larger temperature range. It is probably due to the loss of the remaining water of crystallization. At about 400° to 450° C. (750° to 840° F.) a third expansion begins and continues up to approximately 600° C. (1,110° F.). Above 600° C. (1,110° F.) an increase in temperature causes very little change in length for most of the investments tested. Usually there is a very slight shrinkage, though in most cases this is so small that it is negligible.

TABLE 21.—*Dimensional changes with temperature*

Material		First contraction		Second contraction		Maximum temperature of test	Length change to maximum temperature	Length change after cooling
No.	Plaster	Temperature range	Length change	Temperature range	Length change			
	Per cent	*° C.*	*Per cent*	*° C.*	*Per cent*	*° C.*	*Per cent*	*Per cent*
1	100	140–560	+0.13–−1.90			560	[1]−1.90	−2.82
2 [2]		140–165	+.13–+.03	330–450	+0.09–−0.52	503	[2]−.47	−1.26
3 [3]	56	175–200	+.15–+.11	240–475	+.14–−.64	511	[2]−.61	−1.41
4	40	150–195	+.14–+.11	305–435	+.18–−.43	501	[2]−.35	−1.11
5 [3]	37	140–180	+.14–+.13	300–470	+.22–−.09	511	[2]−.02	−.78
6 [3]	31	150–175	+.11–+.07	315–440	+.20–−.15	510	[2]−.03	−.84
7 [3]	30	160–175	+.15–+.14	345–435	+.22–−.06	623	[1]+.42	−.79
7 [4]	30	150–165	+.15–+.12	350–450	+.25–+.02	650	[1]+.49	−.75
8 [3]		130–175	+.13–+.12	325–415	+.26–+.02	500	[2]+.18	−.62
9 [3]	27	170–185	+.16–+.16	315–415	+.27–+.09	800	+.70	−.61
10 [3]	24	140–170	+.14–+.13	335–425	+.23–+.02	512	[2]+.18	−.64
11 [3]	19	105–155	+.01–−.01	350–400	+.26–+.20	602	[2]+.82	−.42
12	10	92–96	+.09–+.07	300–385	+.29–+.23	499	[2]+.48	−.16
13 [5]		125–230	+.09–−.05	315–370	−.02–−.17	370	[1]−.17	−.74
14 [5]		135–180	+.16–.00	235–505	+.02–−1.92	505	[1]−1.92	−2.65
18 [3]	26	165–180	+.20–+.13	320–405	+.28–+.19	828	[1]+.87	−.56
19 [3]	39	175–235	+.20–+.15			675	[1]+.89	−.47
20	30	195–215	+.15–+.14	335–445	+.22–+.02	720	[1]+.40	−.91

[1] Contracting at maximum temperature of test.
Expanding at maximum temperature of test.
[3] Proprietary investments.
[4] Mixed with 25 per cent less than normal amount of water.
[5] Artificial stone compound.

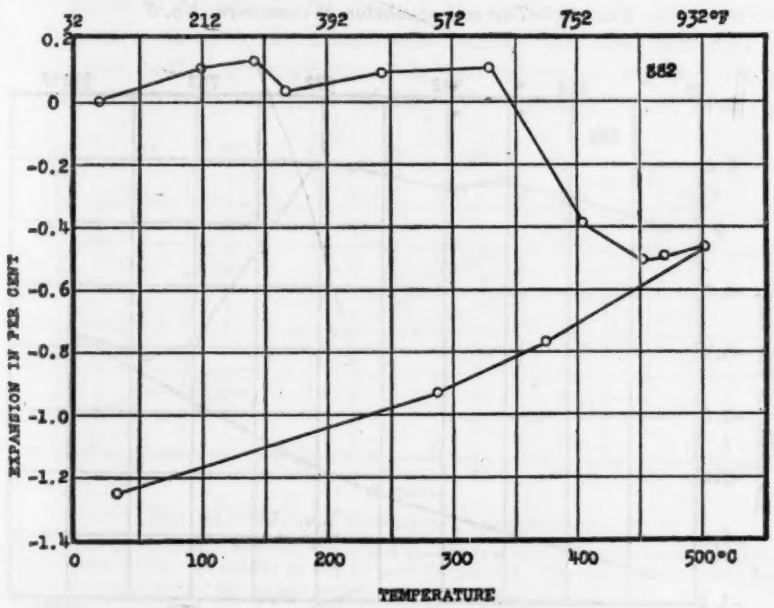

FIG. 47.—*Thermal expansion of investment No. 2*

All of the investments tested contract very markedly when allowed to cool after being heated to temperatures above 125° C. (225° F.). Investments held at any constant temperature, except

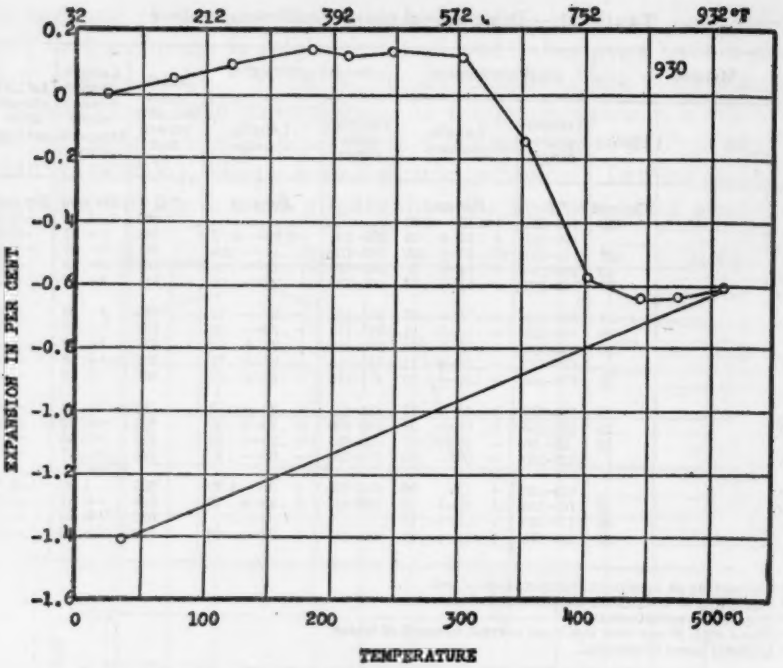

FIG. 48.—*Thermal expansion of investment No. 3*

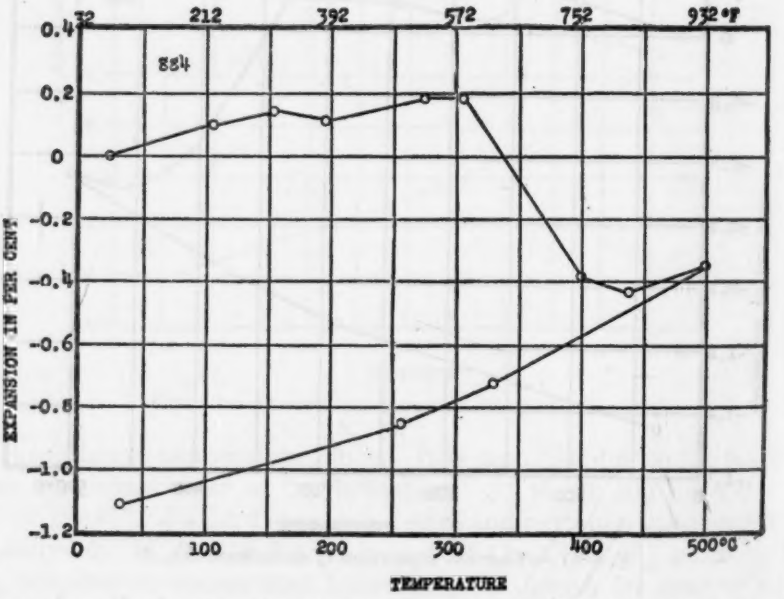

FIG. 49.—*Thermal expansion of investment No. 4*

within the two contraction ranges indicated, did not shrink, even when held for several hours.

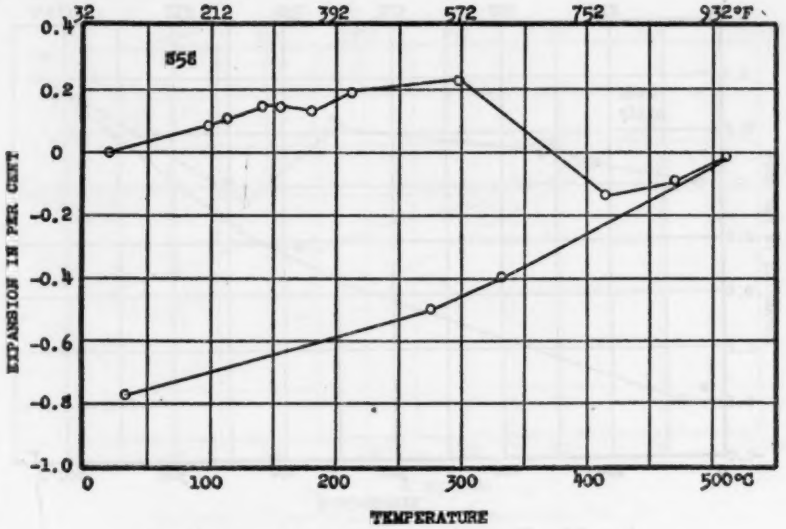

FIG. 50.—*Thermal expansion of investment No. 5*

In Figure 51 are shown the results of two thermal expansion tests on the same sample of investment No. 6. In the first test the sample was heated to approximately 500° C. (930° F.) and allowed to cool to room temperature. The sample was then heated to slightly

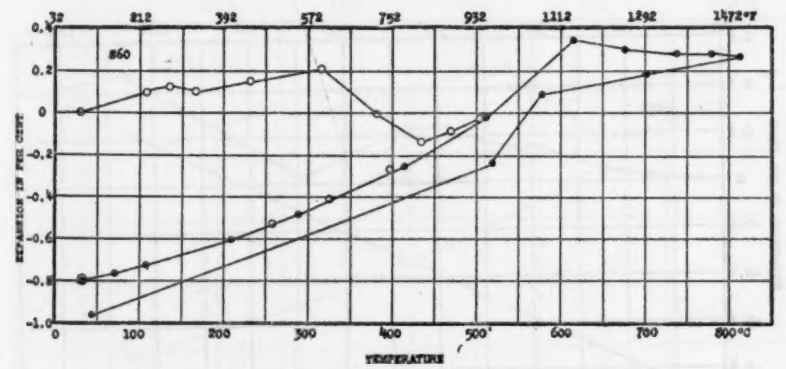

FIG. 51.—*Thermal expansion of investment No. 6*

The light circles represent the observations during the first test, when the sample was heated to approximately 500° C. and allowed to cool to room temperature. The dark circles represent the observations on a second heating and cooling

above 800° C. (1,475° F.) and again allowed to cool to room temperature. After cooling to room temperature following the first heating to 500° C. (930° F.) the investment was 0.8 per cent shorter

than its original length. It will be noted that the first cooling curve very nearly coincides with the second heating curve up to the maxi-

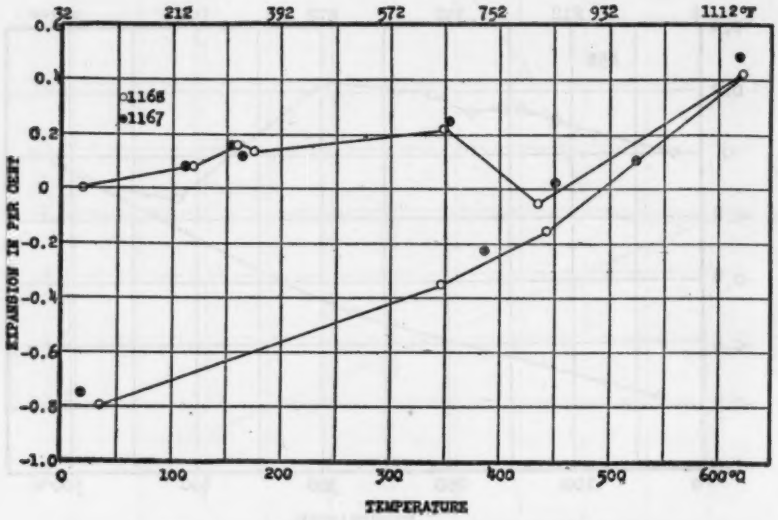

FIG. 52.—*Thermal expansion of investment No. 7*

The light circles represent the expansion of a sample made of 100 g of powder and 46 ml of water, and the dark circles that of a sample made of 100 g of powder and 35 ml of water

mum temperature of the first heating. This indicates that the shrinkage caused by cooling from 500° C. (930° F.) may be corrected by reheating to that temperature. If, however, the investment is

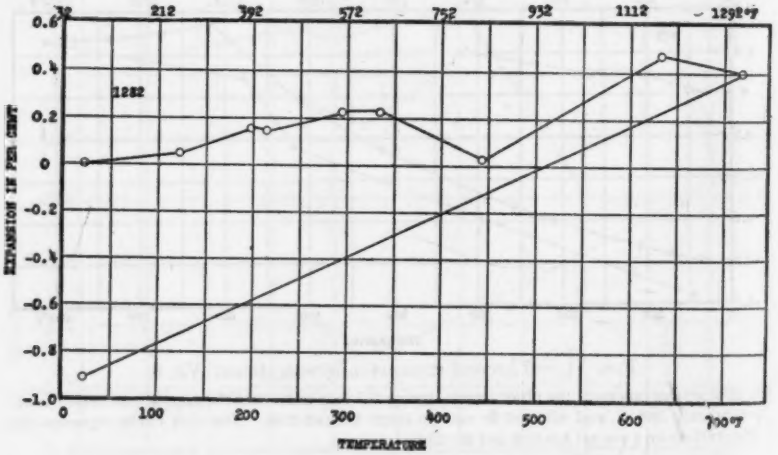

FIG. 53.—*Thermal expansion of investment No. 20*

allowed to cool from 500° C. (930° F.) and is then reheated to a temperature lower than 500° C. (930° F.)—for example, 300° C.

(570° F.)—it will be appreciably shorter than it was when first heated to that temperature.

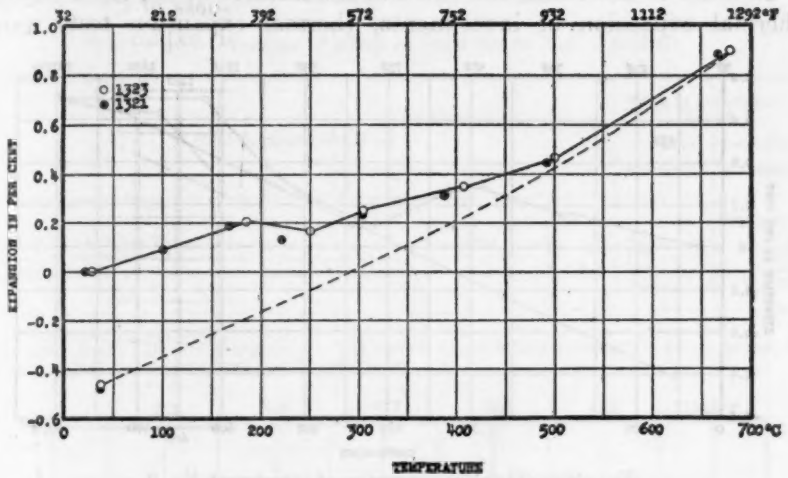

FIG. 54.—*Thermal expansion of investment No. 19*

The light circles represent the expansion of a sample made of 100 g of powder and 32 ml of water, and the dark circles that of a sample made of 100 g of powder and 43 ml of water

In Figure 52 are shown the results of tests on two samples of investment No. 7, one made of 100 g of powder to 46 ml of water and the other of 100 g of powder to 35 ml of water, and in Figure 54

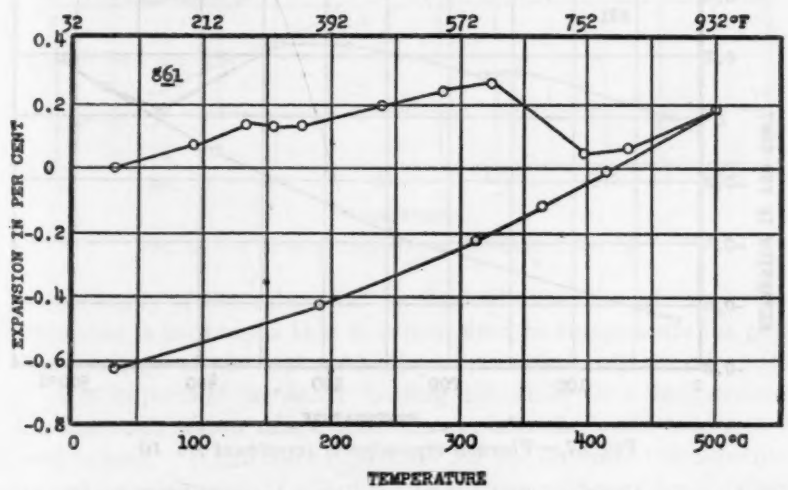

FIG. 55.—*Thermal expansion of investment No. 8*

are shown the results of tests on two samples of investment No. 19, one made of 100 g of powder to 43 ml of water and the other of 100 g of powder to 32 ml of water. It will be noted that these varia-

tions in the amount of water used had no significant effect on the thermal expansion of these investments.

In order to determine the effect of the fineness of the silica on the thermal expansion of investments, thermal expansion tests were

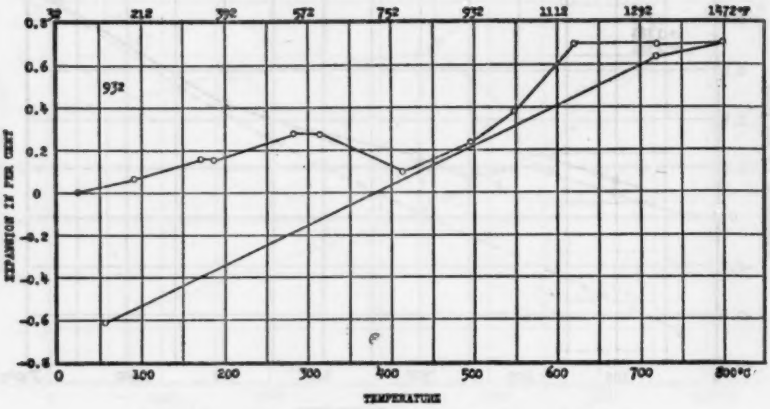

FIG. 56.—*Thermal expansion of investment No. 9*

made on an experimental investment, No. 20, consisting of 30 per cent of plaster of Paris and 70 per cent of a coarse silica. The plaster in this investment is of the same grade as that in investment No. 7, which consists of approximately 30 per cent of plaster and

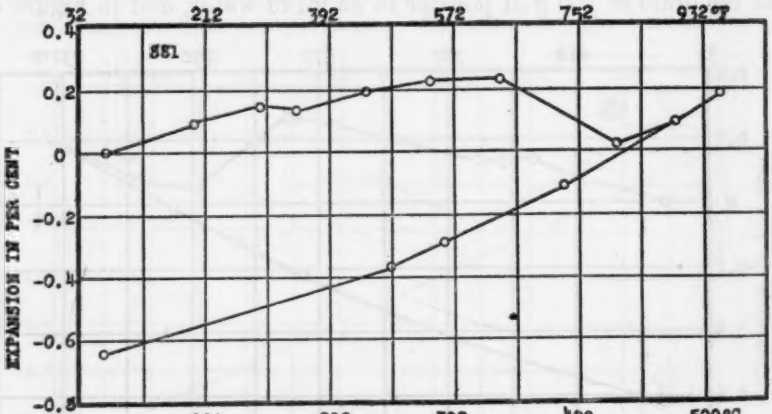

FIG. 57.—*Thermal expansion of investment No. 10*

70 per cent of a fine silica. The fineness[21] of the silica used in these two investments is given in Table 22. The thermal expansion of investment No. 7 is represented graphically in Figure 52 and that of

[21] The author is indebted to John Tucker, jr., of the Bureau of Standards, for determining the fineness of these materials.

investment No. 20 in Figure 53. A comparison of these graphs indicates that the fineness of the silica has very little effect on the thermal expansion of investments of this nature.

TABLE 22.—*Fineness of silica in investments Nos. 7 and 20*

Silica in investment No. 7		Silica in investment No. 20	
		Sieve No.	Retained
	Per cent		*Per cent*
Retained on sieve No. 200	[1] 3	50	1
Retained on sieve No. 325	[1] 8	100	55
20 μ and larger size particles	[2] 52	200	94
		325	99

[1] As determined by wet sieving.
[2] As determined by air current elutriation. The value is approximately equivalent to the percentage of the material that would be retained on a No. 1000 sieve.

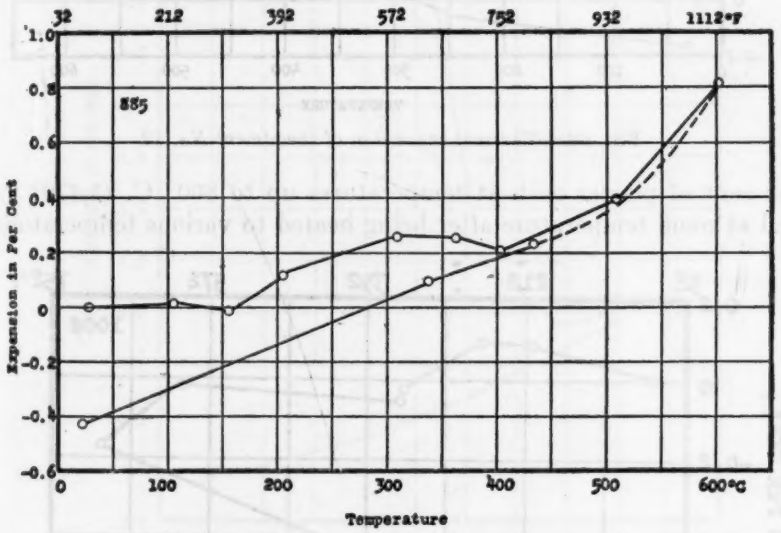

FIG. 58.—*Thermal expansion of investment No. 11*

From a study of the values for the thermal expansion of the investments tested it is obvious that if it is desired to compensate for part of the shrinkage of the cast gold alloys by casting into an expanded mold it is important to avoid heating the mold to a temperature within the contraction range, and to cast into the mold before it is allowed to cool. While the values vary for the different investments, in general an expansion of about 0.2 to 0.3 per cent may be obtained by heating the mold to approximately 300° C. (570° F.). Heating to approximately 600° C. (1,110° F.) will cause dimensional changes ranging from an expansion of more than 1 per cent to a contraction of more than 0.5 per cent, depending upon the investment used.

(c) COMPRESSIVE STRENGTH

Determinations were made of the compressive strength of a plaster of Paris and of two inlay casting investments containing about 30

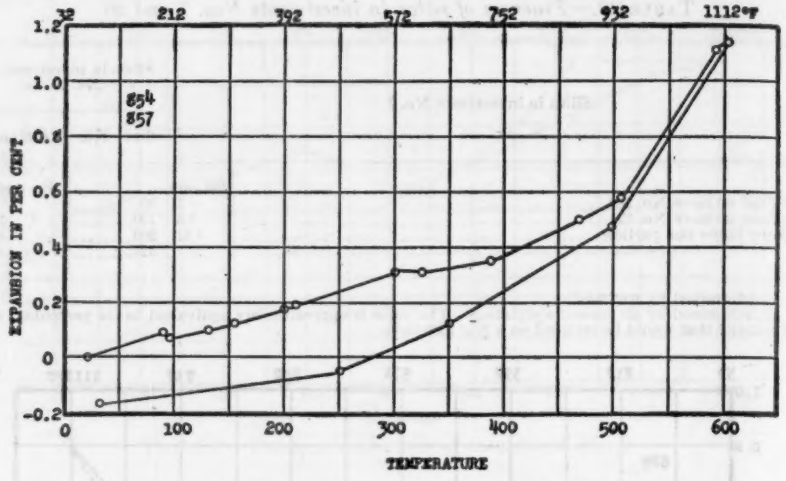

FIG. 59.—*Thermal expansion of investment No. 12*

per cent of plaster each at temperatures up to 800° C. (1,470° F.) and at room temperature after being heated to various temperatures

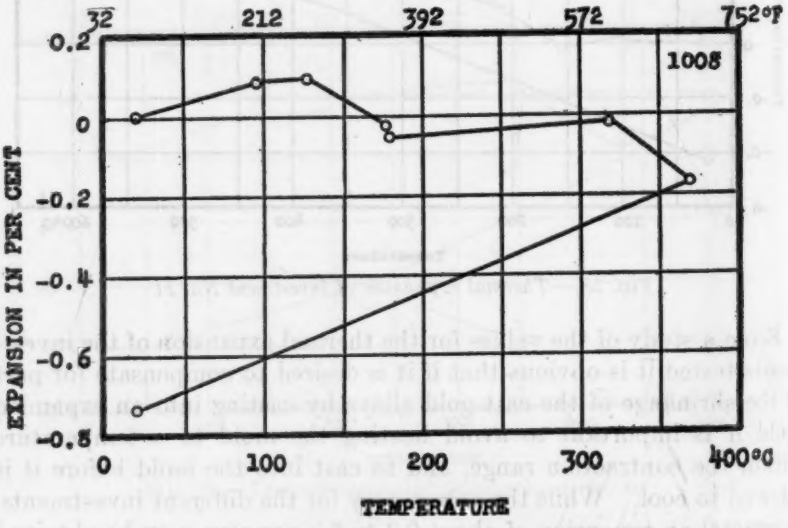

FIG. 60.—*Thermal expansion of investment No. 13*

(Artificial stone compound)

and allowed to cool. A universal testing machine of 2,000 pounds' capacity was used. The load was applied through four screws and

measured by means of a beam and counterpoise. The additional apparatus used in making tests on samples at elevated temperatures is shown in Figure 63. The heating device was a chromel wound, vertical tube electric furnace with rheostats or a voltage regulator for controlling the temperature. The temperature was measured with a thermocouple and petentiometer. Two steel cylinders with ends

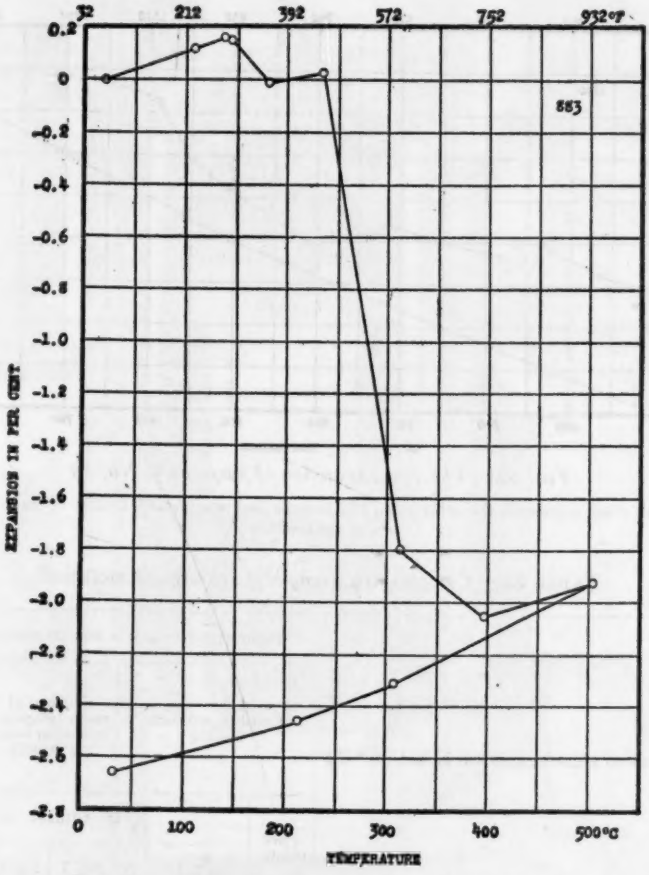

FIG. 61.—*Thermal expansion of investment No. 14*
(Artificial stone compound)

ground flat and parallel, projecting into the ends of the furnace provided means of applying load to the sample.

The samples were cylinders 1.3 inches in diameter and 2 inches long. They were prepared with parallel faces in the mold shown in Figure 64. The type of fracture obtained, also illustrated in Figure 64, indicates that the loading was axial.

The values obtained are given in Table 23. In all cases the values given are the average of several tests. The values for two of the ma-

terials in the green state—that is, before heating—are included for comparison. Except when otherwise stated the proportions used were 46 parts water to 100 parts powder, by weight, for investment Nos. 7 and 18 and 67 parts water to 100 parts powder for the pure plaster. The powder and water were mixed in a mechanical spatulator.

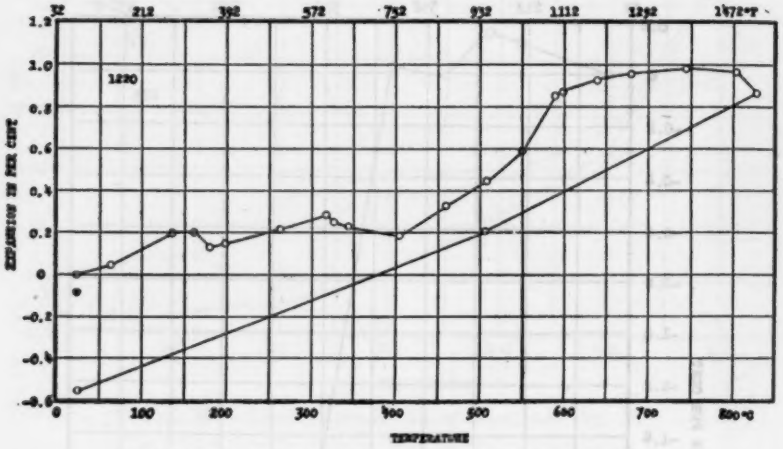

FIG. 62.—*Thermal expansion of investment No. 18*

The dark circle represents the contraction of a sample that was heated to 325° C. and cooled to room temperature

TABLE 23.—*Compressive strength of investment materials*

Temperature to which sample was heated (in ° C.)	Compressive strength in pounds per square inch					
	Crushed without cooling			Crushed at room temperature after cooling rapidly		Crushed at room temperature after cooling slowly
	Pure plaster	Investment				
		No. 7	No. 18	No. 7	No. 18	No. 7
Room temperature	[1] 825	[1] 1 310 [2] 740				
150		160		151		
200	527	178		112		80
300	650	246	390	85	325	72
400		[3] 93 286 [4] 513		89		69
500	620	258		107		83
600	552	199	285	37	165	44
700	662	252	260		215	
800		252	260	39		50

[1] Crushed 3 hours after mixing.
[2] Crushed 6 days after mixing.
[3] Mixed with 25 per cent more than normal amount of water.
[4] Mixed with 25 per cent less than normal amount of water.

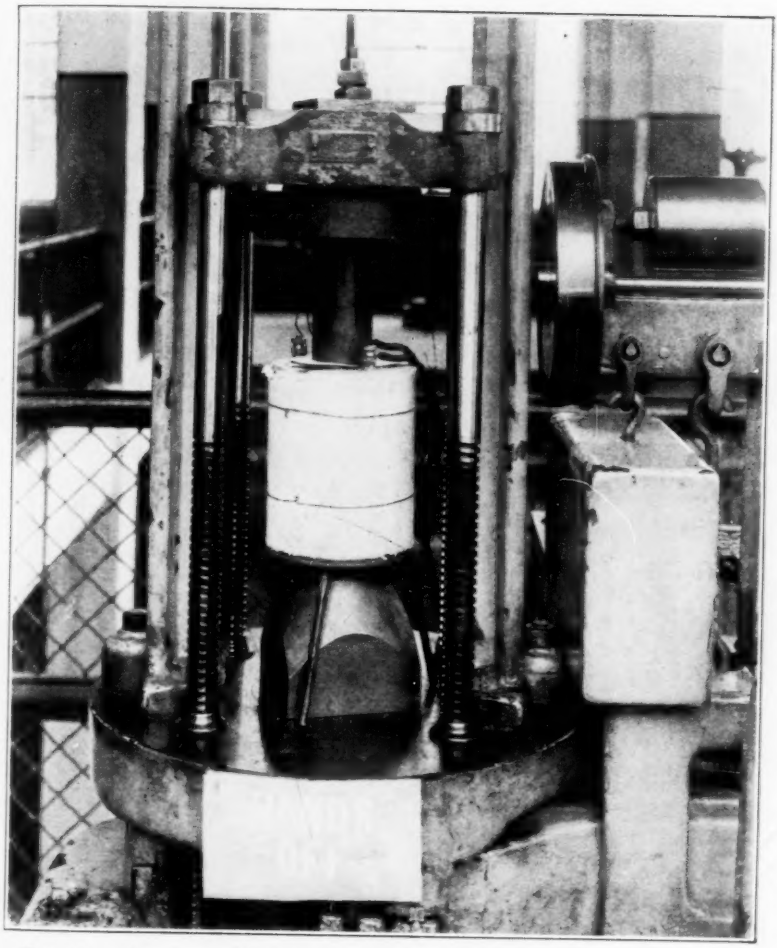

FIG. 63.—*Apparatus for determining compressive strength of investments at elevated temperatures*

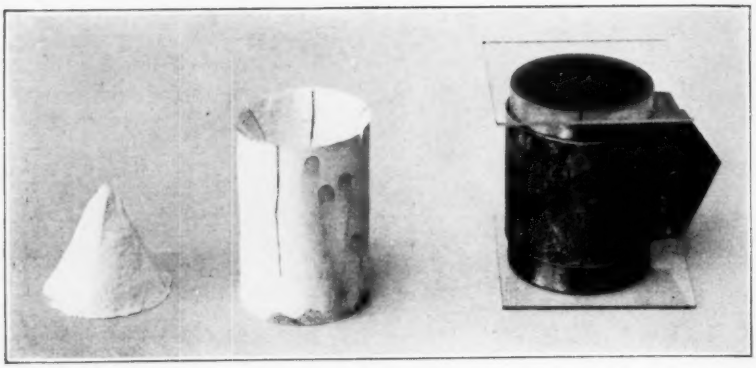

FIG. 64.—*At the right is shown the type of mold in which the samples for determining compressive strength of investments were made. At the left is a crushed sample showing the type of fracture obtained*

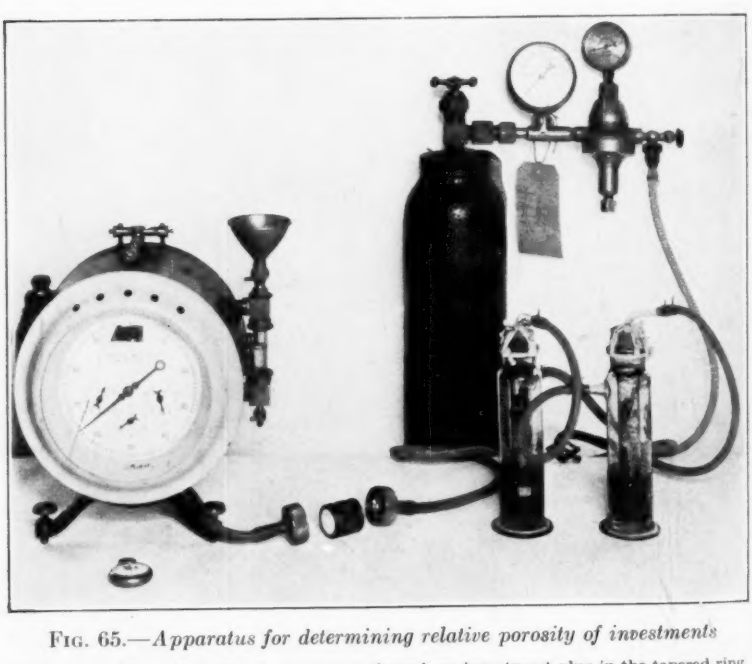

FIG. 65.—*Apparatus for determining relative porosity of investments*

The rate of flow of air at a given pressure through an investment plug in the tapered ring is measured with the gas flow meter and stop watch.

It will be noted that the strength of investment No. 7 (approximate composition 30 per cent plaster-70 per cent silica) drops from about 300 lbs./in.^{2} for the green material, three hours old, to 160 lbs./in.^{2} when heated to 150° C. (300° F.) and crushed hot. As the temperature is raised up to 400° or 500° C. (750° or 930° F.) the strength increases. At 600° C. (1,110° F.) the strength dropped to about 200 lbs./in.^{2}, but at 700° C. (1,290° F.) and 800° C. (1,470° F.) was again near the maximum, which is only slightly below the strength of the green material, three hours old. If this investment is allowed to cool to room temperature after being heated to the various temperatures indicated, the decrease in strength is very marked. It was thought that this decrease in strength might be due to cracking caused by too rapid cooling, but tests on samples allowed to cool slowly in the furnace over a period of several hours showed that the slow rate of cooling caused a still greater loss of strength.

Investment No. 18 is somewhat stronger than investment No. 7, especially at 300° C. (570° F.), and the loss of strength in cooling is not so marked.

The behavior of pure plaster or plaster without any added silica was similar to that of investment No. 7. The strength dropped from 825 lbs./in.^{2} for the green material, three hours old, to 527 lbs./in.^{2} when heated to 200° C. (390° F.). The strength increased slightly at the higher temperatures until, at 600° C. (1,110° F.), there was a marked loss in strength. At 700° C. (1,290° F.) the strength rose to 662 lbs./in.^{2}, which was the maximum value obtained for plaster crushed hot. When samples of pure plaster were cooled from 500° C. (930° F.) or higher, they invariably cracked and fell to pieces.

The effect of varying the proportion of water used with investment No. 7 is shown in the table. When the amount of water was increased 25 per cent, the strength at 400° C. (750° F.) dropped from 286 to 93 lbs./in.^{2} Decreasing the amount of water 25 per cent increased the strength to 513 lbs./in.^{2}

From the results of these tests it may be stated that when the usual inlay casting investment, consisting of about 30 per cent of plaster and 70 per cent of silica, is heated to drive off the moisture and eliminate the wax pattern the loss of strength is comparatively small. If, however, the investment is allowed to cool, the mold becomes very weak and is likely to be distorted by the impact or pressure of the molten gold as it enters the mold.

(d) POROSITY OF INVESTMENTS

In casting into investment molds by any of the methods in common use it is necessary to provide some means of escape for the air in the mold in order that the space may be completely filled by the entering metal. While in some cases this may be satisfactorily

accomplished by properly venting the mold, in general the porosity of the investing material must be relied on wholly or in part. For this reason the relative porosities of various types of investment were determined.

The apparatus developed for making these measurements is illustrated in Figure 65. The determination depends upon measuring the rate of flow of air under a given pressure through a given size plug of the material under test. The procedure is as follows: The investment to be tested is poured into the tapered ring shown in the photograph, allowed to set, and given the desired burning-out treatment. The investment plug is then removed from the ring and coated with a thin film of collodion, except on the ends. The inside of the ring is smeared with heavy grease and the plug replaced. The film of grease prevents leakage of air between the plug and the ring, and the collodion prevents the grease from penetrating into the plug. Air at the desired pressure is applied through the cap with hose connection, and the flow through the plug during a definite time interval is measured by means of a gas-flow meter and a stop watch. The average diameter of the plug is 30 mm and the length 36 mm. The values obtained for a few materials are given in Table 24.

TABLE 24.—*Porosity of investments*

Material		Ratio water to powder by weight	Drying-out treatment	Flow of air in ten-thousandths cubic feet per minute	
No.	Plaster			At 10 pounds per square inch	At 20 pounds per square inch
	Per cent				
3	56	0.52	Held at 250° C. for 1½ hours	21	47
4	40	.43	Heated slowly to 220° C. / Held 220°–240° C. for 3 hours	35	84
7	30	.46	Held at 250° C. for 1½ hours	52	120
7	30	.49	do	73	164
[1] 15	40	.52	do	83	191
[1] 16	50	.54	do	73	176
[1] 17	60	.52	do	53	121
18	26	.46	do	75	187
19	39	.43	do	49	114
19	39	.30	do	25	58

[1] Investment containing 5 per cent of cornstarch.

It was found that, in general, the porosity decreases as the plaster content increases and also as the proportion of water used decreases. Since decreasing the proportion of water increases the strength of the investment, it was thought that it might be possible to improve the usual investments by adding a small amount of some material which would increase the porosity, thus permitting the use of a smaller

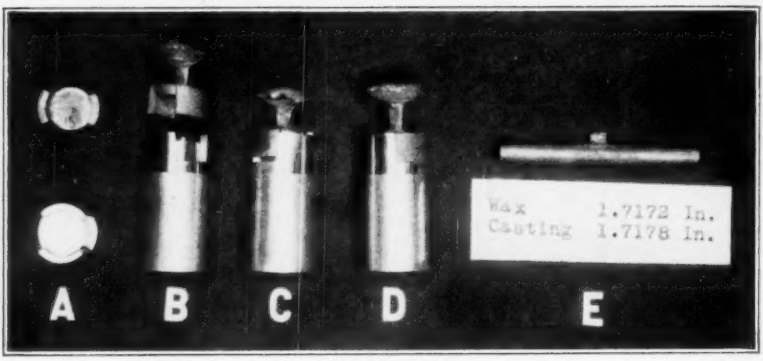

FIG. 67.—*Steel model and gold castings*

A, Top view of model; *B*, Side view of model and casting; *C*, Showing lack of dimensional accuracy in a casting made according to a popular technic; *D*, Showing a casting made by the methods described; *E*, Showing the dimensional accuracy of castings made by these methods.

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amount of water or a higher plaster content. Various materials, such as wood flour, waxes, resins, sugar, starch, and others, were suggested for this purpose. A number of these have been tried and found unsatisfactory for various reasons.

In preliminary tests cornstarch seemed to be a promising material for this purpose. As will be seen from the values given in Table 25 the rate of flow of air through investment No. 17, containing 60 per cent of plaster, 35 per cent of silica, and 5 per cent of cornstarch, was more than double that through investment No. 3, containing 56 per cent plaster, the proportion of water used being 52 ml to 100 g of powder for each investment. However, it was found that investments containing starch are very little, if any, more porous than investments on the market, such as Nos. 18 and 19. For this reason and because the investments containing starch give off a very disagreeable odor and smoke when heated, the general use of these materials is not recommended.

(e) SURFACE ROUGHNESS

In examining a large number of castings made under varying conditions it was found that in practically every case there were a number of small nodules of gold projecting from the surface of the castings. In a few cases, these were very small and could be seen only with the aid of a microscope, but even these small nodules are sufficient to prevent an inlay from properly seating. Preliminary tests indicated that these projecting nodules are due mainly to small air bubbles in the investment, which came in contact with the pattern during the investing process, and that they might be eliminated or at least reduced in number and size by proper mixing and investing methods. Accordingly, various methods of mixing the powder and water and of applying the investment to the wax pattern were investigated. Patterns of a convenient size and shape were invested, the investment being mixed and applied in various ways. After the investment had been dried out and the pattern eliminated the mold was cut open and the investment surfaces which had been in contact with the pattern were examined under a binocular microscope. In this way the relative number and size of the air bubbles in the surfaces were easily detected.

It was found that by carefully applying the investment to the pattern with a small stiff sable or badger hair brush the air bubbles in the surface of the mold could be materially reduced, but were not completely eliminated if bubbles were present in the investment as mixed. The results of numerous tests indicate that air bubbles can be largely eliminated by very thoroughly mixing the water and powder. It was found that this could be accomplished much more consistently and conveniently with a stiff metal blade mechanical mixer of good design than with the usual plaster bowl and spatula.

Another method suggested was that of mixing the investment in vacuum, and the experimental apparatus illustrated in Figure 66 was developed for this purpose. The powder is placed in the container and evacuated. The necessary amount of water is admitted and the mixing accomplished by shaking the container. If a number of balls of some dense material, such as steel, are placed in the container as shown in the drawing, a thorough mixing can be effected very quickly and easily. The results obtained with this apparatus indicate that it is exceptionally effective in eliminating air bubbles from the investment. However, this method of mixing is practicable only when a vacuum pump is available.

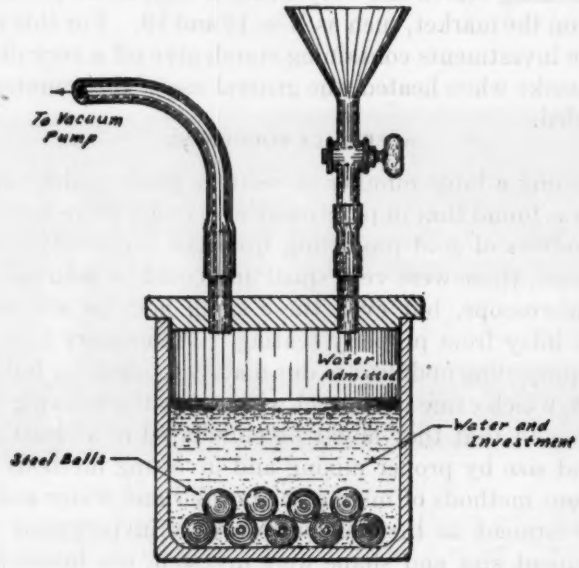

FIG. 66.—*Apparatus for mixing investment in vacuum*

Another form of surface defect often observed was a type of roughness which appeared to be due to an excess of water collecting on the surface of the pattern during or immediately after investing. It was found that by carefully painting the pattern with a thin coat of investment and then sprinkling this coating with dry investment powder, the excess water was absorbed and the roughness largely eliminated.[22] As a further proof that this type of roughness is caused by the presence of excess water, a hypodermic needle was used to deposit small drops of water on the surfaces of patterns invested and sprinkled with dry powder as described, and in every case the roughness reappeared.

[22] Reported in B. S. Tech. News Bul. No. 116, December, 1926.

3. CASTING TO DIMENSION

In order to verify the data obtained on the materials used in the dental casting process and to demonstrate the application of these data in practice, test castings were made to determine the accuracy with which the dimensions of a casting could be controlled. In order to readily demonstrate the accuracy or inaccuracy of the dimensions of the castings produced, and at the same time provide a severe test, it was decided to make castings for a cavity of the mesio-occluso-distal type; that is, one that has both outside and inside dimensions to be fitted. If a casting for this type of cavity is too small, it will not seat in the cavity because it does not fit the outside dimensions, and if it is too large it will not seat because it does not fit the inside dimensions. The walls of the cavity were tapered slightly to facilitate removal of the wax pattern and to provide a means of judging the relative dimensional accuracy of the castings. In order to eliminate as nearly as practicable variations in the dimensions of the cavity, the cavity was prepared in a steel model. In Figure 67 a top view of the model is shown at *A* and side views at *B*, *C*, and *D*.

By referring to the section on the casting shrinkage of gold alloys (p. 908) it will be noted that the average net casting shrinkage for these alloys was found to be 1.25 per cent, and that if no other dimensional variations are introduced in the casting process the castings will be too small by that amount. The obviously available means for compensating for this shrinkage are the thermal expansion of the wax pattern and the thermal and setting expansions of the investment mold. According to the data obtained on pattern waxes (p. 912) and on investments (p. 917) the combined expansions of these two materials may be made to total 1.25 per cent (the amount necessary to compensate for the shrinkage of the cast gold alloy) by a number of different methods. Two examples are cited to illustrate this. If investment No. 18 is used and is mixed in the proportion 100 g. of powder to 40 ml of water, the setting expansion will be 0.21 per cent (see Table 20) and if the investment mold is heated to 600° C. (1,110° F.) the thermal expansion will be 0.87 per cent. (See fig. 62.) The total expansion of the mold is the sum of these two expansions or 1.08 per cent, leaving an expansion of 0.17 per cent to be obtained from the wax pattern. If wax No. 5 is used, it is seen from Figure 43 that 0.17 per cent expansion may be obtained in numerous ways; as, for example, by making the pattern to fit at 33° C. (91° F.) and investing it at 36° C. (97° F.). If the same investment, No. 18, is used mixed with the same proportion of water, the setting expansion again is 0.21 per cent. If the mold is heated to 315° C. (600° F.), the thermal expansion will be 0.28 per cent (see fig. 62) and the total expansion of the mold is 0.49 per cent, leaving an expansion of 0.76

per cent to be obtained from the wax pattern. If the pattern is made of the same wax, No. 5, it is seen from Figure 43 that 0.76 per cent expansion may be obtained by making the pattern to fit at 27° C. (81° F.) and investing it at 40° C. (104° F.).

A number of the possible combinations of materials and methods of manipulation were tested and found to be satisfactory. In Figure 67 a casting made by a popular technic is shown on the model at *C*. It is obvious that this casting does not fit the model. A representative casting made by the second method described above is shown on the model at *D*. This casting was thoroughly washed to remove adhering particles of investment, but was not ground or burnished. The seating of the casting indicates the dimensional accuracy attained. The casting shown at *E*, made by the same method, indicates quantitatively the accuracy with which the original dimensions of the pattern are reproduced in the casting.

It is not intended to recommend the use of any particular materials or any one method. A variety of satisfactory combinations of materials and manipulative procedures are available. There are, however, a few general precautions which should be observed. Care should be taken to obtain a pattern that fits as accurately as possible, as no amount of expansion can compensate for inaccuracies in the pattern owing to lack of adaptation to the walls of the cavity or to distortions introduced during or subsequent to the removal of the pattern from the cavity. It is obvious that in order to obtain the best results it is necessary to exercise careful control of the various manipulative procedures in strict accordance with definite data on the properties of the materials used.

IV. SUMMARY

The physical properties of dental gold alloys used in the wrought and cast states, of investments and of pattern waxes, were investigated. Practicable methods of testing these materials were developed, and these methods and the apparatus used are described. The properties of a large number of representative commercial materials were determined and the values obtained are reported. Especial attention was given to those properties having a direct bearing on the usefulness of these materials in the construction of mechanical dental appliances and to the effects of variations in manipulative procedures. Improvements in methods of manipulation, especially in the dental casting processes and in the heat treatment of gold alloys, were developed. It was found that the dental gold alloys on the market vary widely in their mechanical properties and fusion temperatures as well as in chemical composition. This emphasizes the necessity for selecting suitable materials for specific purposes on the basis of tests of physical properties. The methods of testing developed and de-

scribed herein provide the dental profession and schools with a means of grading and selecting materials on this basis. Some of the more important results of this investigation may be enumerated as follows:

1. In the investigation of dental gold alloys methods of preparing suitable test specimens and special apparatus for determining the mechanical properties of these specimens were developed.

2. It was found that the mechanical properties of many of the gold alloys can be markedly improved by suitable heat treatment. Practical methods of heat treating were developed and described.

3. The porosity or internal voids prevalent in dental gold-alloy castings was found to be due largely to localized shrinkage or occluded gases or both. The usual concentration of these defects adjacent to the sprue may be avoided by the use of a short sprue of large diameter or by providing the mold with a chamber close to the pattern and large enough to supply molten metal to the casting as it shrinks during solidification.

4. Tests for segregation of the constituents of gold alloy castings indicated that no serious defects from this cause are to be expected in the ordinary dental casting processes.

5. It was found that the selective loss of constituent metals or the "unbalancing" of the composition of gold alloys caused by melting is negligible when the melting is done with reasonable care. If the alloys are heated to excessively high temperatures, loss of base metals is likely to occur.

6. The net linear casting shrinkage of an alloy containing 90 per cent gold and 10 per cent copper was found to be approximately 1.25 per cent. No significant variations in this value caused by variations in the temperature of the metal when cast, the temperature of the mold, or the casting pressure were observed. Measurements made on a number of other alloys indicated that no large variations in net shrinkage, caused by the variations in composition of the usual casting golds, is to be expected.

7. The thermal expansions of five inlay pattern waxes and one impression compound were determined. The change in linear dimensions over the temperature range 25° to 40° C. (77° to 104° F.) was found to be 0.4 per cent for the impression compound and to vary from about 0.7 to 0.8 per cent for the pattern waxes tested. Wax patterns were found to be subject to distortion on account of the release of internal stresses on heating. Such distortions can be minimized by working the wax at as high a temperature as possible when making the pattern and by avoiding subsequent overheating.

8. The usual investments for inlay casting expand on setting. This linear expansion is approximately 0.25 per cent.

9. The compressive strength of the usual inlay investments is not seriously affected by heating to temperatures between 200° C.

(390° F.) and 800° C. (1,470° F.). Cooling from these temperatures results in a very marked loss of strength.

10. The above investments may be expanded about 0.2 to 0.3 per cent by heating to 250° to 300° C. (480° to 570° F.). Heating to 350° to 450° C. (660° to 840° F.) results in a contraction, the magnitude of which varies for the different investments. Heating to approximately 600° C. (1,110° F.) will cause dimensional changes ranging from an expansion of more than 1 per cent to a contraction of more than 0.5 per cent depending upon the investment used. Cooling from any of the above temperatures is accompanied by a relatively large contraction. Varying the proportion of water within the usual limits has very little effect on the expansion of these investments. No appreciable effect on the expansion caused by variations in the fineness of the silica in the investments was observed.

11. It was found that by selecting suitable combinations of materials and manipulative procedures a total expansion of the wax pattern and the mold sufficient to compensate for the casting shrinkage of the gold alloys can be obtained. Methods of obtaining this compensation were verified and are described.

12. Two types of roughness of surface of dental castings, causing inaccuracies of dimensions, were observed. It was found that one of these was due to air bubbles in the investment and the other to the collection of water on the surface of the pattern during or soon after investing. The first type can be largely eliminated by thorough mixing of the investment, preferably with a mechanical mixer, or by mixing the investment in vacuum. The latter type can be largely eliminated by painting the pattern with a thin coat of investment and then sprinkling this coating with dry investment powder.

WASHINGTON, June 7, 1928.

USE OF THE UNDER-WATER SPARK WITH THE HILGER SECTOR PHOTOMETER IN ULTRA-VIOLET SPECTROPHOTOMETRY

By H. J. McNicholas

ABSTRACT

The paper describes a device for the operation of a high-voltage electric discharge between metal terminals under distilled water and its use with the Hilger sector photometer in ultra-violet spectrophotometry.

The spark terminals are inclosed in a hard-rubber box, through which a stream of distilled water may be circulated. External adjustments are provided for the length of the spark gap and its position relative to the axis of the optical system.

The effect of the dispersion introduced by the biprism and wedges of the sector photometer is discussed in its relation to the adjustment of the spark; and some modifications in the construction of the photometer are suggested.

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I. PURPOSE AND SCOPE OF PAPER

The high-voltage discharge under water has been used by many investigators as a source of radiant energy in ultra-violet spectrophotometry. Its advantage over arcs and sparks in air or other gases lies in the continuity [1] and uniformity of its spectrum throughout the visible and ultra-violet regions to the limit of transmission of the quartz spectrographs commonly employed in this kind of work. The uniform continuous spectrum is most suitable for quantitative spectrophotometric measurements and enables the accurate location of sharp absorption bands.

This source has been in use at the Bureau of Standards for a number of years in the well-known method of photographic spectrophotometry employing the Hilger sector photometer with a quartz spectrograph. The theory of this method and a description of the apparatus have been given [2] in B. S. Sci. Paper No. 440 (Scientific

[1] Under certain conditions an electrical discharge through hydrogen yields a continuous spectrum, which has been used by others for absorption measurements.

[2] See also papers by Howe, Phys. Rev. (2), 8, p. 674; 1916; and by Tyndall, B. S. Tech. Paper No. 148 Appendix.

Papers of the Bureau of Standards, vol. 18, p. 121; 1922), and the reader is here assumed to be familiar with the general nature of the apparatus and its method of use.

Since the above paper was issued, however, improvements have been made in the construction and operation of the source. Various improvements in the photometric apparatus have been under consideration but, owing to the pressure of other work, have not been effected. In view of the increasing application of quantitative methods to the study of the absorptive properties of materials in the ultra-violet, it is believed that the following description of the improved source, with the accompanying discussion of the photometric apparatus, will be of interest to those contemplating the design and installation of similar equipment.

II. CONSTRUCTION OF SOURCE

In the use of the under-water spark with the Hilger sector photometer certain difficulties arise as a result of the wave-length dispersion along the axis of the spark gap, introduced by the biprism and wedge lenses of the photometer. As explained later, this necessitates a careful adjustment and rigid support of the spark terminals and the use of an adequate length of spark gap in order to obtain and maintain the desired equality between the intensities of the two beams of radiant energy emitted by the spark to the photometer.

The construction of the new source is shown in Figure 1. The spark terminals are inclosed in a hard rubber box, the inside dimensions of which are 75 by 75 by 90 mm. The upper terminal enters the box through a thick hard rubber circular rod, which projects well under the surface of the water before exposing any of the bare metal of the terminal. This is an important detail of the construction, in order to confine the high-voltage oscillatory discharge to the spark gap. When the bare metal is allowed to come in contact with the surface of the water, the discharge tends to follow the surface around to the other terminal.[3] The lower terminal of the spark gap is grounded, as is also the lower terminal of the tesla coil (T, fig. 1) and the whole metal support for the box. The upper terminal of the tesla coil is connected by a carefully insulated wire to the upper well-insulated terminal of the spark gap. Adjustments for the length of the gap are provided, as clearly illustrated in the figure.

The metal used for the terminals is tungsten wire approximately 2 mm in diameter. Molybdenum, brass, and other metals have also been used. The operation of the spark and the continuity of the spectrum are apparently independent of the nature of the metal.

[3] In the original construction of the box this matter was not given careful consideration. As a result, it was later found necessary to alter the construction sufficiently to provide the proper insulation of the upper terminal before a satisfactory operation of the spark was obtained.

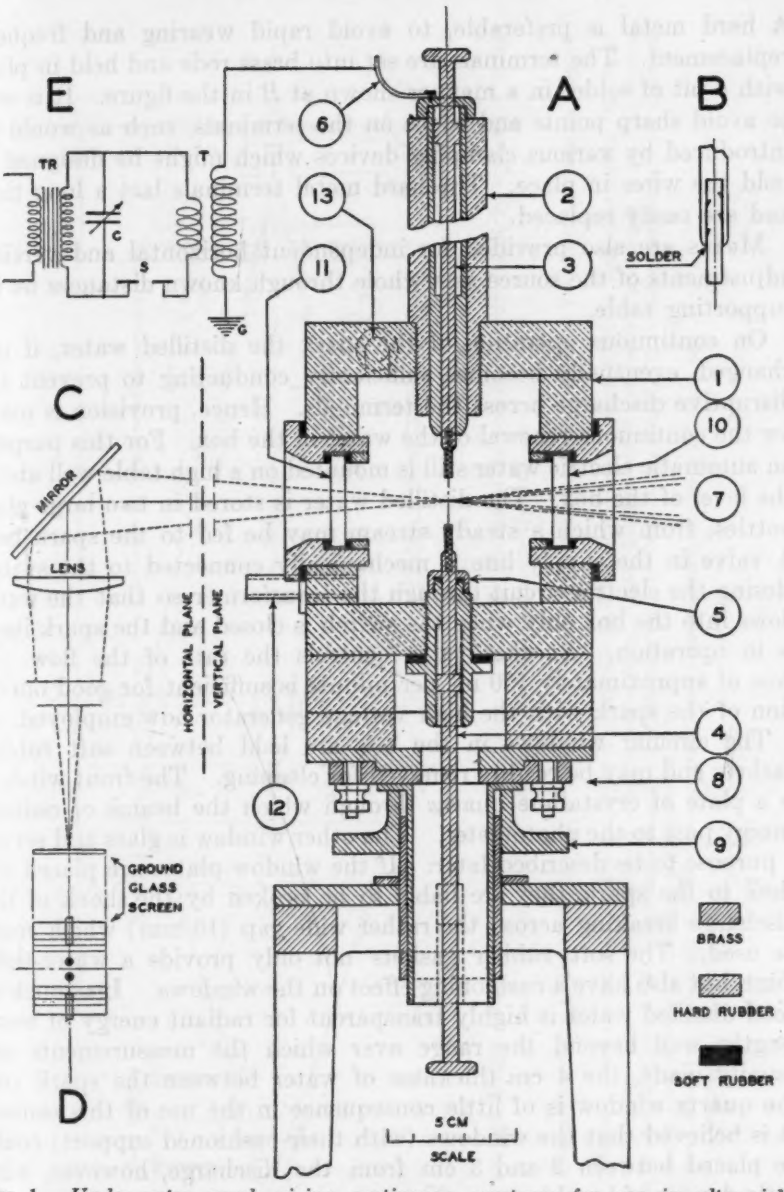

FIG. 1.—*Under-water spark giving continuous spectrum for use in ultra-violet spectrophotometry*

A, vertical median section through center of spark terminals and beams to photometer. (*1*) Hard-rubber box, inside dimensions 75 by 75 by 90 mm. Built up from sheet stock 2 cm in thickness. Plates held together by cement and metal screws. (*2*) Hard-rubber rod 3 cm in diameter. (*3*), (*4*) Brass rods carrying hard-metal terminals of spark gap and adjustable in vertical direction. (*5*) Packing box to prevent leakage of water. (*6*) Electrical connection to upper terminal. Lower terminal and metal parts of base are grounded. (*7*) Beams of radiant energy to photometer. (*8*) Provision for horizontal adjustment of spark box, in direction perpendicular to beams. (*9*) Vertical adjustment of spark box. (*10*) Crystalline quartz window. (*11*) Glass window. (*12*) Inlet for distilled water. (*13*) Overflow tube.
B, showing method for the support of tungsten or other hard metal terminals in brass rods (*3*) and (*4*).
C, Lens and mirror arrangement imaging plane of spark terminals on ground-glass screen.
D, showing images on ground-glass screen of spark terminals and beam sections (for green light) in plane of spark.
E, electrical circuits for operation of spark. (*T*), Tesla transformer. (*S*), primary spark gap. (*C*), variable condenser (set of Leyden jars). (*TR*), Iron-core transformer, 110 to 20,000 volts.

A hard metal is preferable, to avoid rapid wearing and frequent replacement. The terminals are set into brass rods and held in place with a bit of solder in a manner shown at *B* in the figure. It is well to avoid sharp points and edges on the terminals, such as would be introduced by various clamping devices which might be designed to hold the wires in place. The hard metal terminals last a long time and are easily replaced.

Means are also provided for independent horizontal and vertical adjustments of the source as a whole through known distances on its supporting table.

On continuous operation of the spark the distilled water, if unchanged, eventually becomes sufficiently conducting to prevent the disruptive discharge across the terminals. Hence, provision is made for the continuous renewal of the water in the box. For this purpose an automatic electric water still is mounted on a high table well above the level of the box. The distilled water is stored in two large glass bottles, from which a steady stream may be fed to the spark box. A valve in the supply line is mechanically connected to the switch closing the electric circuit through the transformer so that the water flows into the box only when the switch is closed and the spark itself is in operation. Another valve controls the rate of the flow. A flow of approximately 150 ml per minute is sufficient for good operation of the spark with the high voltage generator now employed.

The circular windows in the box are held between soft rubber gaskets and may be readily removed for cleaning. The front window is a plate of crystalline quartz through which the beams of radiant energy pass to the photometer. The other window is glass and serves a purpose to be described later. If the window plates are placed too close to the spark, they are liable to be broken by the shock of the discharge breaking across the rather wide gap (16 mm) which must be used. The soft rubber gaskets not only provide a water-tight joint, but also have a cushioning effect on the windows. Inasmuch as good distilled water is highly transparent for radiant energy of wave lengths well beyond the range over which the measurements are usually made, the 4 cm thickness of water between the spark and the quartz window is of little consequence in the use of this source. It is believed that the windows (with their cushioned support) could be placed between 2 and 3 cm from the discharge, however, with little danger of breaking.

III. WAVE-LENGTH DISPERSION IN OPTICAL SYSTEM OF PHOTOMETER

A diagram of the optical parts of the Hilger sector photometer[4] is shown in Figure 2. Two beams of radiant energy from the spark

[4] The sector photometer here under discussion was built in the shops of the Bureau of Standards and is a duplicate of the Hilger instrument. Any small differences in construction which may exist would not materially affect the present discussion.

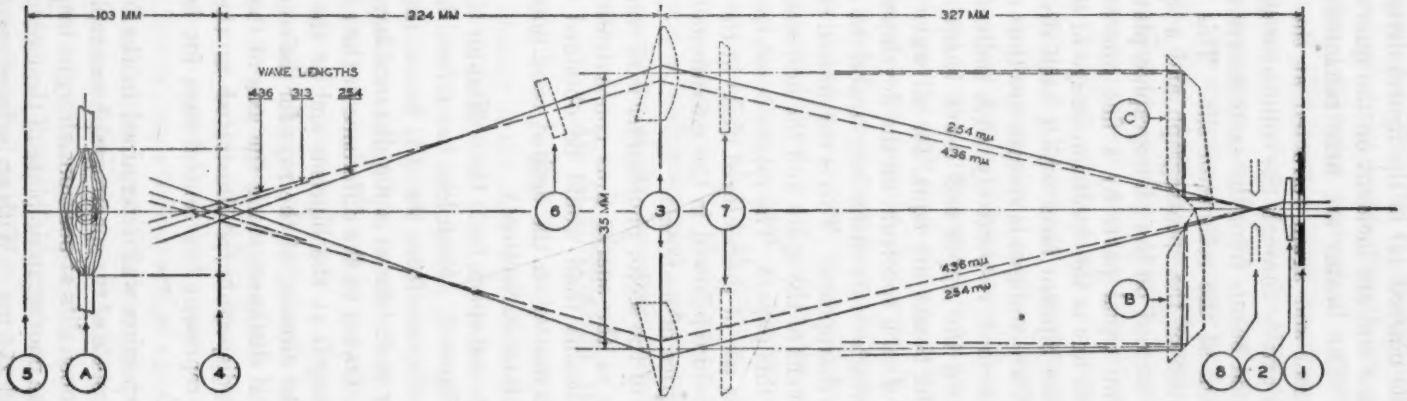

FIG. 2.—*Trace of rays through Hilger sector photometer, showing (primarily) the dispersion at the spark gap introduced by refraction at the biprism and at the wedges on the photometer lenses*

Vertical spread of beams on diagram is drawn to four times the scale of the horizontal distances; hence the dispersion is magnified four times in the diagram. Optical parts are not drawn to scale.

Description of parts: (*1*) Collimator slit of spectograph. (*2*) Biprism, made of crystalline quartz cut with optic axis perpendicular to back plane surface. (*3*) Wedge lenses of photometer. Each is a single piece of crystalline quartz cut with optic axis parallel to axis of lens. Focal lengths of lenses each approximately 16 cm. (*4*) Plane of spark gap and mean position for crossing of beams. (*5*) Approximate plane of foci of collimator slit. (*6*) Transmission sample. (*7*) Variable sectored disks. (*8*) Spark gap between aluminum terminals; used to locate wave-length positions on photographic plate.

A, vertical section through spark gap and through beams of different wave lengths. All dimensions strictly to scale, with 16 mm gap.

B, *C*, suggestions for redesign of photometer. See text.

(which is placed in the plane marked (4) in the figure) diverge from each other in a vertical plane and are incident on the quartz wedge lenses of the photometer. The beams are here refracted toward the axis of the optical system and again refracted at the inclined faces of the biprism to pass axially through the collimator slit of the spectrograph. Two separated beams from the same source are thus combined into a single beam at the collimator slit. This beam is dispersed by the quartz prism of the spectrograph and a spectrum image of the collimator slit formed on the photographic plate. The spectrum is divided into two equal parts by a fine line extending along its entire length. This line is the spectrum image of that part of the intersecting line of the biprism faces which itself divides the slit into two equal parts. Two contiguous spectra are thus obtained on the photographic plate, formed, respectively, with radiant energy entering the instrument along the upper and lower beams. When the intensities of the entrant beams are equal for all wave lengths, the blackening (or density) of each spectrum on the developed photographic plate is the same throughout its entire length, and the dividing line between the two spectra disappears. This is the desired condition to be attained in the adjustment of the spark and the principal matter for further consideration in this paper. The reader is referred to the previous publications for the use of the sectored disks in the entrant beams and the general procedure followed in the measurement of the spectral transmissive properties of materials.

The purpose of the lenses of the sector photometer is to control the cross section of the beams at the spark, thus concentrating more radiant energy into these beams than would be obtained without lenses. The bearing of this matter on the desired conditions of adjustment will be considered later in Section V.

The distances of the lenses and spark from the collimator slit of the spectrograph are given in Figure 2. Each lens has a focal length of approximately one-half its distance from the slit; hence, the conjugate focus of this slit is for each lens at some distance beyond the crossing points of the rays. Owing to the difference in the refraction of rays of different wave length at the biprism and at the wedges on the photometer lenses, the crossing of the rays for different wave length takes place at unequal distances along the axis of the optical system. This wave-length dispersion is illustrated in the figure, where the rays, as drawn, represent the central rays for beams of different wave length.

The magnitude of the dispersion was determined in the following manner: The photographic plate of the spectrograph was replaced by a piece of cardboard having open slits at positions along its length corresponding to positions on the photographic plate of the mercury lines of wave lengths 436, 313, and 254 mμ. With an inclosed mercury arc

lamp mounted behind the cardboard plate, a homogeneous beam of radiant energy of either wave length 436, 313, or 254 mμ could be sent in a reversed direction through the spectrograph and sectored disk photometer. By inserting and exposing strips of photographic plate in the beams at various distances from the biprism to the spark the separation of these beams was recorded for each of the three wave lengths. For the sake of clearness in the representation, the magnitude of the dispersion has been quadrupled in the diagram relative to the other dimensions given therein. Actually, the distance between the two central rays for wave lengths 254 and 436 mμ is approximately 3 mm in the plane of the spark, and the axial distance between the crossing points for these rays is approximately 28 mm.

When the spark is placed at a position along the axis corresponding to the crossing of rays of a wave length in the neighborhood of 300 mμ, both beams to the spectrograph for this same wave length are then taking radiant energy from the same area of the spark. For longer and shorter wave lengths, however, it is obvious that each beam collects its radiant energy from different areas of the spark. The discharge is not continuous, of course, but consists of a rapid succession of sparks following different paths across the terminals and presenting an appearance (due to the persistence of vision) much the same as represented at *A* in the figure. An equality of the intensities of the two beams to the spectrograph for wave lengths in the far ultra-violet or visible spectral regions must depend, therefore, on the proper averaging of the discharges through the separated sections of each beam.

IV. ADJUSTMENT OF SPARK

The best average position of the spark on the axis of the system is at the crossing of the rays for a wave length somewhat shorter than 313 mμ. It is obvious that the terminals of the gap should also be placed in the plane of dispersion (vertical). To obtain an equality of the intensities of the two beams for all wave lengths, it is necessary to use a sufficient length of spark and to accurately maintain the positions of the terminals relative to the axis of the system and the plane of dispersion for the two beams. The greater the length of gap that may be used the less sensitive will be the adjustments. This is apparent from a consideration of the diagram of the spark at *A* in Figure 2; for as the individual sparks wander over the faces of the terminals, or persist for a time at any one point of either terminal, the chance of obtaining a time-averaged equality of the discharges through the separated sections of each beam is greater when the terminals are farther removed from the corresponding sections of the beams. As might be expected, the vertical adjustment of the spark is more sensitive than either horizontal adjustment. These adjustments can be made quite stable and permanent with the apparatus herein

employed when a 16 mm gap is used. The stability of the adjustments is increased very appreciably when the gap is increased from 14 to 16 mm. This gap is about the limit that can be used, however, with the high-voltage generator at present installed. It is believed that still better results would be obtained with a slightly larger gap and a more powerful generator of higher voltage. An excess voltage for the spark and greater capacity in the primary oscillatory circuit would undoubtedly lead to steadier operation of the under-water spark and avoid the necessity for a high degree of purity in the water.

The desired position of the spark gap on the axis of the optical system is known from the diagram of Figure 2, after a correction is applied for the small refraction of the beams in passing from air to water. This adjustment need not be accurate, however. A glass lens and silvered-glass mirror are permanently mounted as shown at *C* in Figure 1, with the spark terminals and a ground glass screen placed in conjugate planes of the lens. These planes are selected to give approximately unit magnification. When an incandescent lamp is set up at the photographic plate end of the spectrograph, in proper position to send a beam of green or blue-green light in reverse direction through the instrument, a cross section of the two beams in the plane of the spark terminals may then be seen on the ground glass along with an image (unmagnified) of the terminals. The picture presented to the eye is illustrated at *D* in Figure 1. By means of the horizontal and vertical adjustments provided for the spark box, the spark terminals may be readily lined up in the plane of dispersion at the spark and the length of the gap adjusted from time to time as the terminals gradually wear away. If a sufficient length of gap is used, this adjustment will be accurate enough to give the desired result; but if for any reason a shorter gap must be used, it may be necessary to take a series of exposures on the photographic plate, each for a slightly different vertical or horizontal position of the spark, and the best position chosen by an examination of the developed plate.

V. SUGGESTIONS FOR IMPROVEMENT OF PHOTOMETRIC SYSTEM

In the preceding sections the construction of the present equipment is described along with a discussion of certain conditions to be fulfilled in its operation. Some modifications in the construction will now be considered, by means of which the required conditions of operation may be realized in an easier and more satisfactory manner. With due consideration for the essential requirements to be met in the optical system, many of the difficulties experienced with this photographic method may be avoided. The particular combination of lenses and dispersion in the present apparatus is inconsistent with these requirements. In the following discussion we are chiefly con-

cerned with the cross section of the beams at the spark and with the linear wave-length dispersion along its (vertical) axis. It is assumed that the wedge lenses are properly adjusted, so that the central rays, as represented in Figure 2, intersect on the central axis of the photometric system.

As a first consideration, let the focal lengths of the photometer lenses be increased so that the conjugate foci of the collimator slit fall at considerably greater distances from the axis of the spark, and the cross sections of the beams at the spark are as represented in Figure 3, *B*, for some wave length in the visible or far ultra-violet. Let the spark terminals be placed so that the entire discharge takes place through the common overlapping sections of each beam. Then, under this condition, each individual spark must send an equal quantity of radiant energy along each beam to the spectrograph. The absolute position of the spark terminals now ceases to be a matter

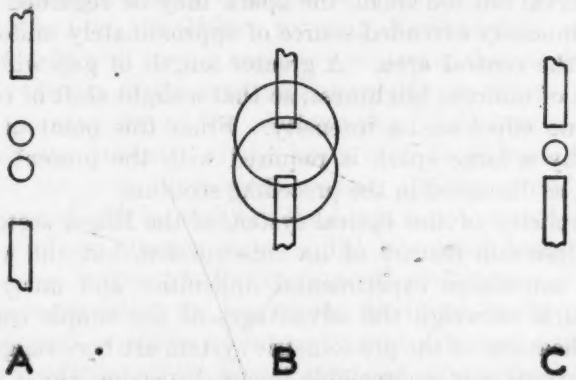

FIG. 3.—*Vertical section through beams at spark gap, corresponding to different constructions of the photometric system*

for careful adjustment. They need only be maintained within the overlapping sections of the beams.

With this arrangement, however, the spectrum obtained on the photographic plate would not be strictly continuous, for radiant energy emitted by the portions of the spark within 3 or 4 mm of the terminals contains some characteristic lines of the metal superposed on the otherwise continuous spectrum; but this would not be a serious disadvantage if the total spark length is not too small. The chief disadvantage of this arrangement would lie in the decreased intensity of radiant energy entering the spectrograph along each beam. To make the most efficient use of the source, its area should completely cover the cross section of the beam.

A more effective means of obtaining the desired ease and permanence of the adjustment is to eliminate the linear wave-length dispersion along the axis of the spark. Then the separated sections

shown in Figures 2, *A*, and 3, *A* (also 3, *B*) would coincide for all wave lengths as illustrated at *C* in Figure 3, and the best focal length of the photometer lenses would be such as to bring the conjugate foci of the collimator slit slightly beyond the plane of the spark. A shorter spark gap could then be used, thus concentrating the discharge through the coincident sections of the beams, with a maximum gain in their time-averaged intensity. As in the arrangement represented by Figure 3, *B*, an accurate adjustment of the spark terminals would not be required. Furthermore, with the shorter spark, a lower voltage would be sufficient for its operation, and by use of a higher voltage primary transformer (*T*, fig. 1) the inefficient Tesla coil could be eliminated. It would be well to use a somewhat larger spark, however, than is indicated in Figure 3, *C*, in order to provide for slight displacements or changes in convergence when a sample is introduced into either beam. When the individual discharges are averaged over a time interval not too small, the spark may be regarded as a somewhat continuously extended source of approximately uniform brightness over the central area. A greater length of gap will provide a larger area of uniform brightness, so that a slight shift of either beam will have no effect on its intensity. From this point of view it is evident why a large spark is required with the present equipment (fig. 3, *A*), as discussed in the preceding sections.

The simplicity of the optical system of the Hilger sector photometer is a desirable feature of its construction, but the wave-length dispersion introduces experimental difficulties and uncertainties in its use which outweigh the advantages of the simple construction. Two modifications of the photometric system are here suggested, each of which avoids any appreciable linear dispersion along the axis of the spark by the use of rhombs to obtain the desired separation of the two beams from the spark to the spectrograph.

One method of use of the rhombs is illustrated at *B* in Figure 2. The angular dispersion introduced at the biprism is unchanged by passage through the rhomb, but if the wedge on the lens at (*3*) is cut down to approximately half its present angle an equal but opposite angular dispersion is introduced into the system which practically annuls the linear dispersion along the axis of the spark. A proper choice of angles and distances could be made to give a practically achromatic system, as far as conditions at the spark are concerned. With this system it would be advantageous to place the sectored disks on the spark side of the wedge lenses, leaving a distance of 20 to 25 cm between the rhomb and the wedge lens for the insertion of the sample. If a parallel beam through the sample is desired, an additional lens could be conveniently mounted on the rhomb support. The advantages of this construction would undoubtedly fully warrant the insertion of the additional optical parts.

An alternative suggestion is indicated by the use of a different type of rhomb at C (fig. 2). In this case the angular dispersion introduced by the biprism is annulled at the entrance surface of the rhomb, leaving only a slight and negligible separation of the two rays as represented in the figure. The rays could then be brought to the spark by a similar use of rhombs. This optical system would be quite similar to that employed in the Lewis sector photometer.[5]

It may be noted that each of the suggested modifications of the Hilger sector photometer preserves the convenient biprism and wave-length spark arrangement as shown at (*8*) in the figure. The biprism is unexcelled for the production of a fine disappearing line between the two contiguous spectra on the photographic plate. This, in turn, is an advantage in the accurate reading of the plates. It is important that the entire optical system of the photometer (including the biprism) be firmly mounted on a single metal base.

In both modified designs suggested above either the Lewis vane-sector method or the Hilger rotating sectored-disk method could be used equally well for the necessary control of the relative intensities of the two beams in the spectrophotometric procedure. In the first method the exposure of the photographic plate is continuous (with time), and the intensity of the beam may be decreased directly by decreasing the area of its cross section. In the second method, on the other hand, the intensity of the beam is not altered directly, but, by the use of the rotating sectored disk, the total time of exposure is decreased by intermittently cutting off the beam. The question hence arises regarding the blackening produced on the photographic plate by equal products of intensity and exposure time, when the exposure is continuous in the one case and intermittent in the other. The reader is referred to the papers previously cited and to more recent papers by Baly, Morton, and Riding,[6] and by Ley and Volbert,[7] for a description and experimental comparison of the two photometric methods. These comparisons do not show any discrepancies between the two methods which are greater than other experimental uncertainties in the measurements. The sectored disks are simpler and more accurate from a mechanical standpoint. They may easily be made large enough and with sufficient accuracy to avoid significant errors in the setting of the angular openings to values as low as 1 per cent.

WASHINGTON, June 6, 1928.

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[5] J. Chem. Soc. Lon. Trans., **115**, p. 312; 1919.
[6] Roy. Soc. Proc., **113**, p. 709; 1927.
[7] Zeit. f. Phys. Chem., **130**, p. 308; 1927.

REACTION OF WATER ON CALCIUM ALUMINATES

By Lansing S. Wells

ABSTRACT

The four calcium aluminates ($CaO.Al_2O_3$, $3CaO.5Al_2O_3$, $5CaO.3Al_2O_3$, $3CaO.Al_2O_3$) have been made, and the mechanism of their reaction with water has been studied. The tricalcium aluminate, $3CaO.Al_2O_3$, reacted so rapidly with water that changes in the composition of the resulting solutions could not be followed. The other calcium aluminates, as well as a high alumina cement, reacted with water to form metastable and supersaturated monocalcium aluminate solutions in the early periods. The metastable solutions decomposed as the reaction proceeded with the precipitation of varying amounts of hydrated alumina and crystalline hydrated tricalcium aluminate, with attendant increases in both the pH and molar ratio, CaO/Al_2O_3, in the resultant solutions. The constitution of the aluminate solutions has been discussed. Calculations based upon electrometric measurements and chemical analyses indicate that the aluminate in solution is the calcium salt of monobasic aluminic acid. A study of the subsequent changes in the aluminate solutions, attended by increasing concentrations of calcium hydroxide, indicates that a hydrated tetracalcium aluminate may be formed in solutions where the pH value is greater than 12.0. An electrometric titration study of aluminum chloride and calcium hydroxide and an investigation of the calcium chlor-aluminates are described.

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I. INTRODUCTION

Investigations [1] of the ternary system, lime-alumina-silica, have established the constitution of all definite combinations of lime and alumina, lime and silica, alumina and silica, and lime, alumina, and silica. They have shown that lime can combine with alumina at high temperatures only in the following molecular proportions: $3CaO.5Al_2O_3$, $CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $3CaO.Al_2O_3$. Tricalcium aluminate ($3CaO.Al_2O_3$) appears to be the only aluminate in Portland cement of normal composition and normal properties. The other main constituents of such cements are tricalcium silicate ($3CaO.SiO_2$) and the beta form of dicalcium silicate ($2CaO.SiO_2$). The monocalcium aluminate ($CaO.Al_2O_3$) and the 3:5 calcium aluminate ($3CaO.5Al_2O_3$) occur in the cements characterized by a high alumina content. Such cements have the property of hardening in a short time and acquiring meanwhile very high strengths. The cementing qualities of the calcium aluminates have been reported by Bates; [2] the properties of the calcium silicates and calcium aluminates occurring in normal Portland cement, by Bates and Klein; [3] and the hydration and hydrolysis of the compounds which may occur in Portland cement, by Klein and Phillips, [4] and by Lerch and Bogue, [5] respectively.

These investigations have indicated that the setting of all calcium aluminates is accompanied by the formation of hydrated tricalcium aluminate with or without hydrated alumina. Recently some preliminary experiments, undertaken at the bureau, had indicated that the setting of the calcium aluminates and high alumina cements might be closely related to their reaction with water in the formation of metastable and supersaturated solutions of calcium aluminates. From these solutions the hydrated tricalcium aluminate and hydrated alumina precipitated. It was decided, therefore, to investigate this reaction and obtain more information as to its mechanism.

The first part of this paper concerns not only the chemical composition and pH values of these solutions as they are formed in the early period of setting, but also the changes which they undergo as the solutions pass from a metastable condition to one of equilibrium. Then, at this point, a further study was also made of subsequent changes in the aluminate solutions attended by increasing concentrations of calcium hydroxide, a product of the hydrolysis of the cal-

[1] Rankin and Wright, "The ternary system lime-alumina-silica," Am. J. Sci., **39**, p. 1; 1915; Bowen and Greig, "The system Al_2O_3-SiO_2," J. Am. Cer. Soc., **7**, p. 238; 1924; Hansen, Dykerhoff, Ashton, and Bogue, "Studies of the system lime-alumina-silica. The composition $8CaO+Al_2O_3+2SiO_2$," J. Phys. Chem., **31**, pp. 607-615; 1927.

[2] Bates, Cementing Qualities of the Calcium Aluminates, B. S. Tech. Paper No. 197.

[3] Bates and Klein, Properties of the Calcium Silicates and Calcium Aluminate Occurring in Normal Portland Cement, B. S. Tech. Paper No. 78.

[4] Klein and Phillips, Hydration of Portland Cement, B. S. Tech. Paper No. 43.

[5] Lerch and Bogue, "Studies of the hydrolysis of compounds which may occur in Portland cement," J. Phys. Chem., **31**, p. 1627; 1927.

cium silicates. The second part of the paper deals with an electrometric titration study of aluminum chloride and calcium hydroxide and an investigation of the calcium chlor-aluminates.

II. REACTION OF WATER ON THE CALCIUM ALUMINATES

1. PREPARATION OF COMPOUNDS

The following calcium aluminates were made by W. Lerch by the methods developed in this laboratory:[6]

3:5 calcium aluminate	$3CaO.5Al_2O_3$
Monocalcium aluminate	$CaO.Al_2O_3$
5:3 calcium aluminate	$5CaO.3Al_2O_3$
Tricalcium aluminate	$3CaO.Al_2O_3$

For the preparation of these binary compounds, chemically pure calcium carbonate and alumina were mixed in the proper proportions with a little water, molded into bars, and burned in an up-draft, gas-fired kiln for four hours at a temperature[7] of $1,350 \pm 20°$. To obtain a homogeneous product the material was ground, remolded, and reburned at the same temperature. No free lime was found in any of these reburned aluminates either by the White's test[8] or by the method of titration with ammonium acetate.[9] Microscopic examinations[10] showed the resultant material to be homogeneous and of the desired constitution. The materials were then ground to a degree of fineness such that about 90 per cent passed a No. 200 sieve.

2. APPARATUS AND SOLUTIONS EMPLOYED

For the determination of the hydrogen-ion concentration of the aluminate solutions, the electrometric method was used. The potentiometric system consisted of a Leeds and Northrup type K potentiometer and type R galvanometer with properly shielded switchboard and wiring. The Weston cell values were certified by the electrical division of this bureau.

The saturated KCl-calomel electrode was used in the hydrogen ion set-up. Its use does not necessitate the protection from contamination by the saturated KCl used in making liquid junctions required in the use of normal and tenth-normal electrodes. A gooseneck siphon, constricted at the tip, connected the tightly stoppered bottle containing the saturated KCl of the liquid junction with the hydrogen electrode vessel of 100 ml capacity. By this arragement the contamination of the solutions was reduced to a minimum, and any inherent error was probably very small and constant. The stem of a separa-

[6] B. S. Tech. Papers Nos. 43, 78, and 197; Lerch and Bogue, J. Phys. Chem., 31, p. 1627; 1927.
[7] All temperatures in this work are expressed in the centigrade scale.
[8] A. H. White, J. Ind. Eng. Chem., 1, p. 5; 1909.
[9] Lerch and Bogue, Ind. Eng. Chem., 18, p. 739; 1926.
[10] Made by F. W. Ashton, of this bureau.

tory funnel, filled with saturated KCl, led into the bottle containing the saturated KCl of the liquid junction. By opening the stopcock of this funnel the gooseneck siphon could be washed free of any contamination from the solution of the hydrogen electrode vessel.

A simple wire type of hydrogen electrode was used. By bubbling hydrogen through a small hole in the side of the glass tube containing the platinized wire, the solution of the electrode vessel was surged about the electrode. A small hole in the stopper of the electrode vessel served as an outlet for the hydrogen. By this arrangement air was conveniently expelled from the electrode vessel and excluded during the measurement. In fact, all operations were made with protective measures against contamination by atmospheric carbon dioxide. The hydrogen used was electrolytic hydrogen supplied in tanks. It was passed through a series of wash bottles containing solutions of alkaline potassium permanganate, alkaline pyrogallol, mercuric chloride, and a solution similar to that contained in the electrode vessel, respectively.

All materials were purified with great care, and the system was checked against standard buffered solutions and was found to conform to the standard as recommended by W. M. Clark.[11]

The cells and the solutions to be studied were kept in an air thermostat well insulated by an air space of 1 inch between double glass walls. There were also double glass doors through which, when opened, the apparatus could be reached. Heating of the air was effected by bare nichrome resistance wire strung on an open frame of asbestos board. A small electric blower, with well-insulated piping, mounted outside the thermostat provided for a rapid circulation of air. The heater was placed at the air exit of this blower. The thermostat maintained a temperature of $30 \pm 0.05°$ by means of a toluene-mercury regulator connected to an electric control similar to the device of D. J. and J. J. Beaver,[12] but modified for operation with a U. X. 201-A radio tube.

In accordance with custom, the hydrogen ion concentration is expressed in this paper in terms of Sørensen's pH, which is defined by the relation $pH = \log \frac{1}{[H^+]}$. As all electrometric measurements were made at 30°, the pH of the solutions was calculated from the formula

$$pH = \log \frac{1}{[H^+]} = \frac{E.\ M.\ F.\ (\text{observed}) - 0.2437}{0.06011}$$

where the *E. M. F.* is expressed in volts.

[11] W. M. Clark, Determination of Hydrogen Ions, Williams & Wilkins, Baltimore; 1922.
[12] D. J. and J. J. Beaver, J. Ind. Eng. Chem., 15, p. 359; 1923.

3. METHOD OF PROCEDURE

Preliminary experiments indicated that metastable calcium aluminate solutions were formed during the reaction of water with the anhydrous calcium aluminates or high alumina cement. It was, therefore, decided to study not only the chemical composition and pH of these solutions as they were formed in the early period of the setting processes, but also to follow the changes which they underwent as the solutions passed from a more or less metastable condition to one more nearly approaching equilibrium.

The procedure followed in this study was to shake the anhydrous calcium aluminate or high alumina cement with distilled water in the proportion of 50 g of solid to 1 liter of water for a given time and then filter the mixture rapidly through a Büchner funnel. Samples of these filtrates were taken at once for chemical analyses and for pH determinations. In the analyses the solutions were made slightly acid with hydrochloric acid and the aluminum was precipitated as the hydroxide and ignited to the oxide according to Blum's method.[13] In the analyses of the more concentrated aluminate solutions the aluminum hydroxide was dissolved and reprecipitated before ignition. The calcium was precipitated as the oxalate, ignited to constant weight in a platinum crucible, and weighed as the oxide.

After the samples had been taken the filtered solutions were set aside in well-stoppered flasks for further observations. On standing, part of the lime and alumina precipitated from the clear solutions in changing from a metastable condition to one more nearly approaching equilibrium. After two weeks the resulting mixtures were filtered. Samples of these filtrates were also taken for chemical analyses and for pH determinations. The precipitates were washed with alcohol and ether and dried in a desiccator containing anhydrous calcium chloride. The dried material was examined with the petrographic microscope [14] and analyzed chemically for lime, alumina, and water (loss on ignition). It was preferable to make the analyses for alumina and lime on samples other than those used for the determination of loss on ignition, since heat converted a portion of the alumina to a form difficultly soluble in acids.

4. REACTION OF WATER ON MONOCALCIUM ALUMINATE ($CaO.Al_2O_3$)

Klein and Phillips [15] have shown, by petrographic methods, that monocalcium aluminate starts to hydrate almost immediately upon the addition of water. Bates [16] has pointed out that the high alumina cements, which contain this aluminate, develop most of their high

[13] W. Blum, Determination of Aluminum as Oxide, B. S. Sci. Paper No. 286.
[14] Examinations made by Dr. H. Insley, of this bureau.
[15] B. S. Tech. Paper No. 43.
[16] B. S. Tech. Paper No. 197.

strengths within 24 hours. It has also been observed that the reaction of water on the other calcium aluminates progresses rapidly. For these reasons the study herein described was particularly concerned with those reactions occurring within the first few hours.

Accordingly, mixtures of anhydrous monocalcium aluminate and distilled water in the proportion of 100 g of solid to 2 liters of water were shaken in flasks to prevent setting. After a definite interval of time one of these mixtures was filtered through a Büchner funnel, and later, when another definite period of time had elapsed, a second mixture was filtered. This process was continued until all had been filtered. In this way successive definite increments of time were represented by each filtration. Filtering required between 5 and 10 minutes. After the samples had been taken the clear filtrates were set aside in well-stoppered flasks for further observations. Since these clear metastable solutions were metastable in varying degrees, it was necessary to examine them immediately after filtering from the reaction mixture. Thus, the determination of the pH values of the samples of the filtered solutions were started at once, as it was observed that a precipitation of lime and alumina from the clear metastable filtrates began, in some cases, within two or three hours after filtering. Then, at the end of two or three weeks, the mixtures resulting from the decomposition of the metastable solutions were also studied.

The data obtained in these investigations are recorded in Tables 1 and 2. In Table 1 the figures in the first column refer to the number of the experiment, and the second column gives the time of contact of the monocalcium aluminate with water before filtration. The columns designated by A (columns 3, 5, 7, 9, 11, and 13) contain the data as determined and calculated with respect to the solutions obtained directly upon filtering from the reaction mixtures and are, therefore, descriptive of conditions of the clear filtrates prior to any subsequent decomposition after filtering. In the columns designated B (columns 4, 6, 8, 10, 12, and 14), there are recorded the results of the same measurements as described under A. However, in the case of B the measurements were made upon the solutions (numbered the same as those of A in column 1), but after an elapse of two or three weeks, whereas the results and calculations tabulated under A refer to the same original solutions at the time immediately following filtration as above described. A comparison of the data of each column A to those of its adjacent column B shows, therefore, the changes which have occurred in the filtered solutions in passing from a more or less metastable condition to one more nearly approaching equilibrium and with an attendant precipitation of some of the alumina and lime.

TABLE 1.—*Composition and pH of aluminate solutions*

TABLE 1.—*Composition and pH of aluminate solutions from monocalcium aluminate ($CaO.Al_2O_3$)*

No.	Time of contact of $CaO.Al_2O_3$ with water before filtering	Total alumina in solution, g Al_2O_3 per l		Total lime in solution, g CaO per l		Molar ratio CaO/Al_2O_3 in solution		Lime in solution in excess of $CaO.Al_2O_3$, g CaO per l		Observed E. M. F. of solutions at 30°		pH of solutions at 30°		Ratio of lime in solution in excess $CaO.Al_2O_3$	Ratio of hydroxyl-ion concentration
		A	B	A	B	A	B	A	B	A	B	A	B		
		Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	$\frac{(CaO)_A}{(CaO)_B}$	$\frac{[OH^-]_A}{[OH^-]_B}$
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	15 minutes	2.1850	0.2500	1.2930	0.4455	1.08	3.21	0.0912	0.3080	0.9165	0.9481	11.19	11.72	0.296	0.300
2	30 minutes	2.3655	.2550	1.3970	.4320	1.08	3.08	.0912	.2917	.9186	.9492	11.22	11.73	.312	.310
3	1 hour	2.3500	.2460	1.3730	.4135	1.07	3.06	.0805	.2782	.9179	.9484	11.21	11.72	.290	.311
4	2 hours	2.2000	.2415	1.2880	.4005	1.06	3.01	.0780	.2677	.9182	.9483	11.21	11.72	.291	.316
5	4 hours	2.2350	.2420	1.2910	.4155	1.05	3.08	.0617	.2824	.9157	.9466	11.18	11.69	.218	.306
6	5 hours	2.0910	.2530	1.1960	.4060	1.04	2.84	.0459	.2668	.9179	.9474	11.21	11.70	.172	.323
7	6 hours	.9445	.2445	.6085	.4320	1.17	3.21	.0891	.2975	.9246	.9494	11.32	11.74	.300	.387
8	1 day	.4500	----------	.4165	----------	1.68	----------	.1690	----------	.9389	----------	11.56	----------	----------	----------
9	3 days	.3170	----------	.4560	----------	2.61	----------	.2816	----------	.9453	----------	11.67	----------	----------	----------
10	7 days	.2680	----------	.4620	----------	3.13	----------	.3148	----------	.9487	----------	11.73	----------	----------	----------
11	14 days	.2400	----------	.5165	----------	3.90	----------	.3746	----------	.9498	----------	11.74	----------	----------	----------
12	28 days	.2550	----------	.5050	----------	3.21	----------	.3648	----------	.9510	----------	11.76	----------	----------	----------
13	420 days	.1600	----------	.4715	----------	5.36	----------	.3835	----------	.9509	----------	11.76	----------	----------	----------

Accordingly, columns 3 and 4 give the alumina in solutions, as grams Al_2O_3 per liter, directly upon filtering and at equilibrium, respectively, as previously described, and columns 5 and 6 the lime in the corresponding solutions as grams CaO per liter. Column 7 shows the molar ratio, CaO/Al_2O_3, in solution directly upon filtering as calculated from the data of columns 3 and 5, and column 8 gives this ratio in the resultant equilibrium solutions as calculated from the alumina and lime in columns 4 and 6. Column 9 gives the lime, as grams CaO per liter in excess of monocalcium aluminate, obtained by subtracting from the lime of column 5 the calculated quantity of lime which will combine with the alumina of column 3 as a calcium aluminate of the composition, $CaO.Al_2O_3$. Column 10 gives this excess of lime, computed in the same manner, from the data of columns 6 and 4. Column 11 gives the observed E. M. F., as determined with the hydrogen-ion set-up, of the solutions (A) containing the alumina of column 3 and the lime of column 5, and column 12 the observed E. M. F. of the corresponding solutions (B) at equilibrium which contain the dissolved alumina of column 4 and the dissolved lime of column 6. Columns 13 and 14 contain the pH values calculated from the observed E. M. F. determinations of columns 11 and 12, respectively. The data of the last two columns (15 and 16) will be discussed later. In the light of the above description the subsequent tables, which contain the results of the reaction of water on the other aluminates, will be self-explanatory.

In Figure 1 the quantities of alumina and lime (recorded in columns 3 and 5 and expressed as grams Al_2O_3 and CaO per liter, respectively), dissolved in water, are plotted against the time (in hours) of contact of the aluminate with water. The pH values of the solutions, recorded in column 13, are also plotted against this time.

From the data of columns 3 and 5 of Table 1, as plotted in Figure 1, it is seen that the reaction of water on monocalcium aluminate progresses rapidly. The quantity of both alumina and lime dissolved by the water attained a maximum in 30 minutes and then gradually decreased until about five hours had elapsed. Further shaking resulted in a rapid decrease, which, in turn, became less as time progressed. An apparent state of equilibrium was reached only after several weeks had elapsed.

It is interesting to observe (column 7, Nos. 1 to 7, inclusive) that anhydrous monocalcium aluminate reacted with water in the early periods to form calcium aluminate solutions with a molar ratio, CaO/Al_2O_3, of approximately 1. The pH of these solutions (columns 13, Nos. 1 to 7, inclusive) was very nearly 11.20. At the later periods (Nos. 8 to 13, inclusive), the molar ratio of CaO/Al_2O_3 in solution had increased, with a simultaneous increase in the pH, until the point pH 11.75 was reached, even though the actual quantities of both

alumina and lime in solution decreased. It should be noted (columns 9 and 13) that the increase in pH is accompanied by a corresponding increase of the lime in solution in excess of that calculated to be in combination with the alumina in solution as monocalcium aluminate. A more detailed discussion of this relation will be presented later in this paper.

Turning now to a consideration of the determined and calculated data of columns B of Table 1 in comparison to those of columns A of the same table, it can be seen that changes identical to those described above also took place in the more or less metastable solutions

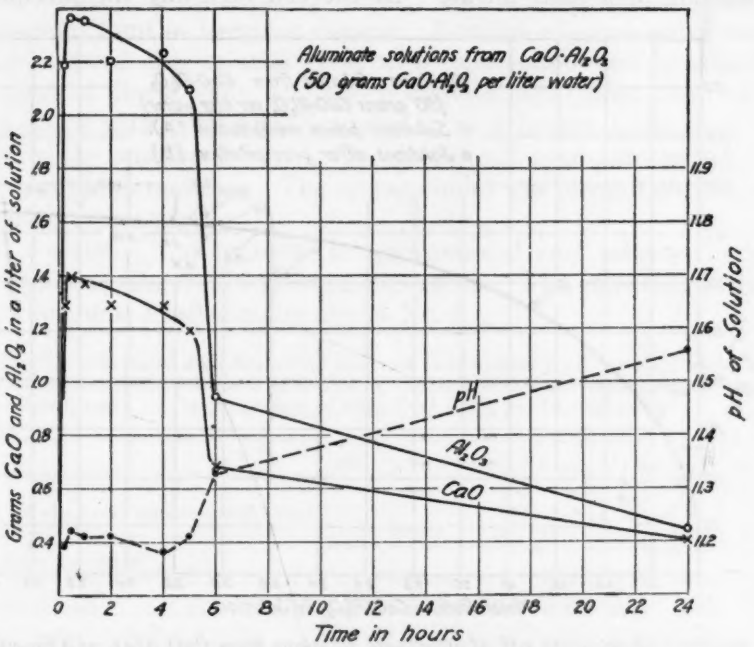

FIG. 1.—*Showing the composition and pH of aluminate solutions from $CaO.Al_2O_3$ as functions of the time of contact with water*

which had been filtered from the reaction mixtures and subsequently had approached equilibrium on standing. A portion of the alumina and lime had precipitated from the clear metastable filtrates (Nos. 1 to 7, inclusive, of columns 3 and 5, respectively), leaving "equilibrium" solutions similar in composition (Nos. 1 to 7, inclusive, of columns 4 and 6, respectively) to those obtained when the anhydrous monocalcium aluminate had been left in contact with water for long periods (Nos. 10 to 13, inclusive, of columns 3 and 5, respectively). The molar ratio of lime to alumina increased as the metastable solutions approached equilibrium on standing, as can be noted from a comparison of the values of Nos. 1 to 7, inclusive, of column 7 to

those of column 8. This also was accompanied by an increase in pH (column 14) to about 11.75, the approximate value obtained for the solutions filtered from the reaction mixtures at the later periods (Nos. 10 to 13, inclusive, of column 13). In Figure 2 the pH values of all of the solutions are plotted against the molar ratio of lime to alumina, CaO/Al_2O_3, in these solutions.

Table 2 contains the chemical analyses of the material precipitated, at the end of two weeks, from the filtered metastable calcium aluminate solutions. Precipitation of this material started from the first six of these solutions within two or three hours after filtering and the obtaining of a clear filtrate. At the end of a day the precipitate

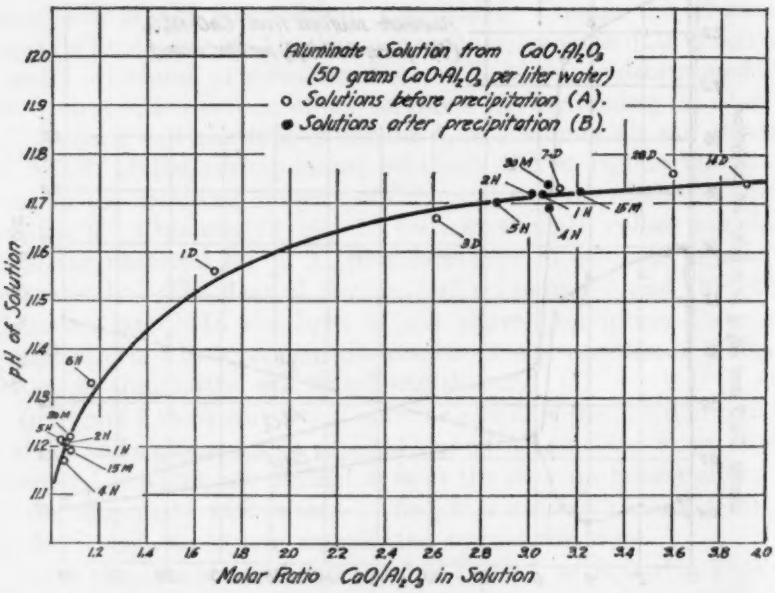

FIG. 2.—*Showing the pH of aluminate solutions from $CaO.Al_2O_3$ as a function of the molar ratio CaO/Al_2O_3 in solution*

covered the bottom of the flask to a depth of about 0.5 cm. Two or three days later small spherulites of crystals appeared on the walls of the flasks. These spherulites, in turn, were covered gradually by a thin film of amorphous material. Also, at the end of this two-week period, when the mixtures were filtered a portion of the material adhered so firmly to the walls of the flasks that it could not be loosened even by vigorous shaking. This loss of material in filtering probably accounts for the differences in the molar ratio of lime to alumina in the precipitate as calculated from the chemical analyses of the material recovered and that as computed from the analyses of the aluminate solutions in the metastable condition (A) and at "equilibrium" (B). In either case, however, the molar ratio of CaO/Al_2O_3 in the precipi-

tate is less than 1.0. This indicates that the precipitate was composed either of a calcium aluminate hydrate with a molar ratio, lime to alumina, less than 1.0, or else was a mixture of hydrated alumina and a more basic calcium aluminate hydrate.

Microscopic examination showed that all samples were composed wholly of the following three phases:

A. A crystalline phase in flat, hexagonal plates with the refractive indices as follows: $\omega = 1.535 \pm 0.004$, $\epsilon = 1.515 \pm 0.005$. The plates were uniaxial negative. The spherulites consisted of radiating aggregates of these crystals.

B. Amorphous material, apparently colloidal aggregates, often in spheroidal form in irregular clumps. Portions of these areas sometimes showed the uniaxial cross as in spherulites and in colloidal portions of fibers. The amorphous material sometimes occurred in thin flakes with polyhedral boundaries, as if broken away from the sides of the containing vessel. It was difficult to obtain the index of the amorphous material. The average index was about 1.48, but was a variable quantity.

C. Calcite. This occurred in aggregates of very minute crystals seldom exceeding 5 μ in greatest dimension. This appeared in very small amounts in all samples except No. 3.

TABLE 2.—*Chemical analyses of the material precipitated from the clear metastable calcium aluminate solutions prepared by shaking anhydrous monocalcium aluminate with water in the proportion of 50 g $CaO.Al_2O_3$ per liter of water*

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Time of contact of aluminate with water before filtering	15 min.	30 min.	1 hr.	2 hrs.	4 hrs.	5 hrs.	6 hrs.
Analysis of precipitate:							
Per cent CaO	17.48	19.28	18.90	17.09	17.52	17.16	(1)
Per cent Al_2O_3	40.72	42.80	42.28	40.19	39.86	40.40	(1)
Per cent H_2O	42.33	37.51	39.00	42.30	42.60	43.78	(1)
Total	100.53	99.59	100.18	99.58	99.98	101.34	
Molar ratio CaO/Al_2O_3 in the precipitate from above analyses	0.780	0.819	0.813	0.773	0.825	0.772	
Molar ratio CaO/Al_2O_3 in the precipitate computed from analyses of solutions (A and B) before and after precipitation	.743	.820	.822	.820	.749	.726	0.458

[1] Too small amount for analysis.

From the chemical analyses and the petrographic examination it is apparent that the material is composed of amorphous hydrated alumina, of varying refractive index, and a hydrated calcium aluminate occurring in hexagonal plates. The refractive indices of these plates are in fair agreement with those given by Klein and Phillips for tricalcium aluminate hydrate in their revised data presented in an unpublished note to P. H. Bates, of this laboratory. Their revised refractive indices are $\omega = 1.520 \pm 0.003$ and $\epsilon = 1.504 \pm 0.003$ and serve to correct their previous values, as given on page 8 of Bureau

of Standards Technologic Paper No. 48, $\epsilon = 1.552 \pm 0.003$ and $\omega = 1.535 \pm 0.003$. They found further that the hexagonal plates were uniaxial negative rather than uniaxial positive. More recently Pulfrick and Link [17] have obtained a crystalline hydrated tricalcium aluminate of the composition $3CaO.Al_2O_3, 7H_2O$ as hexagonal plates which are uniaxial negative. The refractive indices which these authors give, for sodium light, are $\omega = 1.538 \pm 0.0015$ and $\epsilon = 1.523 \pm 0.0015$.

Comparing the optical properties of the crystalline phase in the material as precipitated from the unstable solutions with the revised data of Klein and Phillips for tricalcium aluminate hydrate, it is seen that the crystals, in both cases, occur in flat hexagonal plates, are uniaxial negative, and within the limits of experimental error exhibit the same double refraction. The optical properties agree even better with those of Pulfrick and Link. The refractive indices of these different hydrated crystals, however, differ slightly. This is not surprising, since very thin crystals of this character have such large surfaces that the adsorbed water may be a source of error in the determination of the refractive indices. The data of Table 2 show the percentage of water, as determined as loss on ignition. Both the degree of hydration and adsorption of water may also account for the varying index of the amorphous hydrated alumina.

The small quantity of calcite found in the precipitated material undoubtedly resulted from slow carbonation after the equilibrium mixtures were filtered, since no carbonate was found directly upon filtering.

From this study it would appear, therefore, that, as the reaction of water with monocalcium aluminate progresses, there may be formed more or less metastable and supersaturated calcium aluminate solutions from which hydrated alumina and crystalline hydrated tricalcium aluminate precipitate as equilibrium subsequently is approached. The fact that the aluminate solutions apparently attain the same equilibrium, whether left in contact with the monocalcium aluminate for long periods or whether filtered from the reaction mixtures in the early periods and then allowed to approach equilibrium on standing, indicates that the two solid phases mentioned above may be formed during the "setting" of monocalcium aluminate. It does not permit any conclusions to be drawn as to the relative importance of the above reactions in the actual setting of monocalcium aluminate, nor does it exclude the possibility of the formation of other products in the unfiltered mixtures. This investigation, however, may help to explain the mechanism of the formation of hydrated alumina and hydrated tricalcium aluminate, as noted by Klein and Phillips in their study of the reaction of water with monocalcium aluminate.

[17] Kolloid-Z., 34, p. 117; 1924.

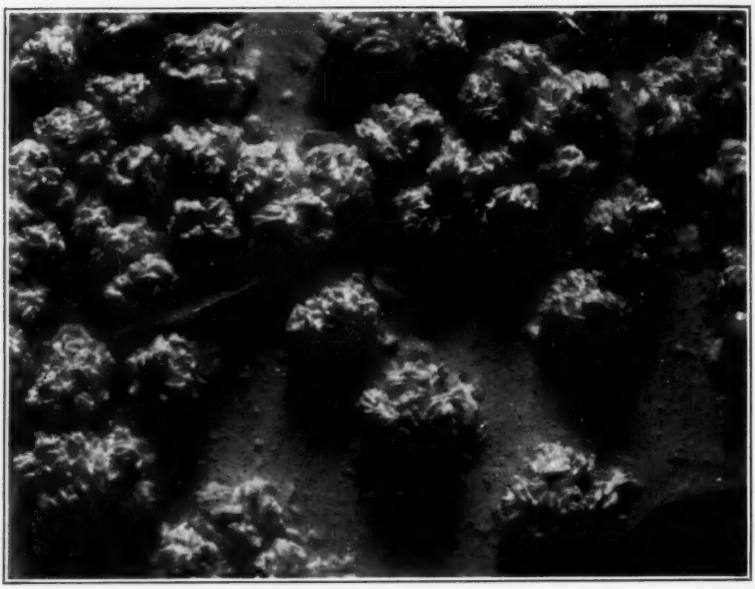

FIG. 3.—*Clusters of hexagonal plates of tricalcium aluminate hydrate imbedded in and partially covered with a thin film of hydrated alumina.* (×9.)

These two solid phases precipitated slowly from solution 7 of Table 1 in passing from a metastable condition to one more nearly approaching equilibrium

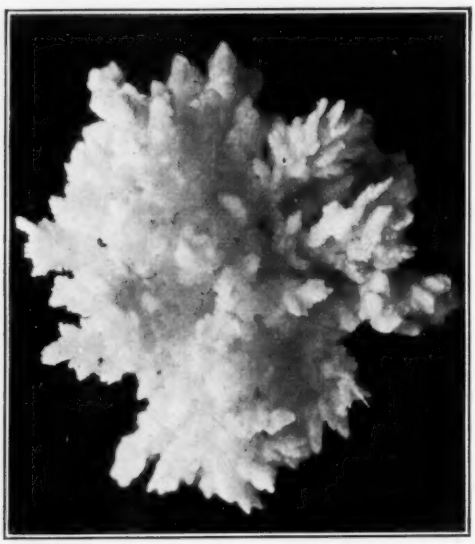

FIG. 4.—*Large individual cluster of hexagonal plates of tricalcium aluminate hydrate removed from the walls of the flask and photographed with a black background.* (×9.)

5. REACTION OF WATER ON THE 3:5 CALCIUM ALUMINATE ($3CaO.5Al_2O_3$)

The method of procedure used in the study of the 3:5 calcium aluminate was essentially the same as that already described in the investigation of the reactions of monocalcium aluminate.

In Table 3 there are tabulated the composition and pH of the more or less metastable aluminate solutions (columns A) obtained from the 3:5 calcium aluminate directly upon filtering from the reaction mixture and the data relative to these same solutions at the end of two weeks (columns B). In Figure 5 the quantities of alumina and lime in solution (recorded in columns 3 and 5 and expressed as grams Al_2O_3 and

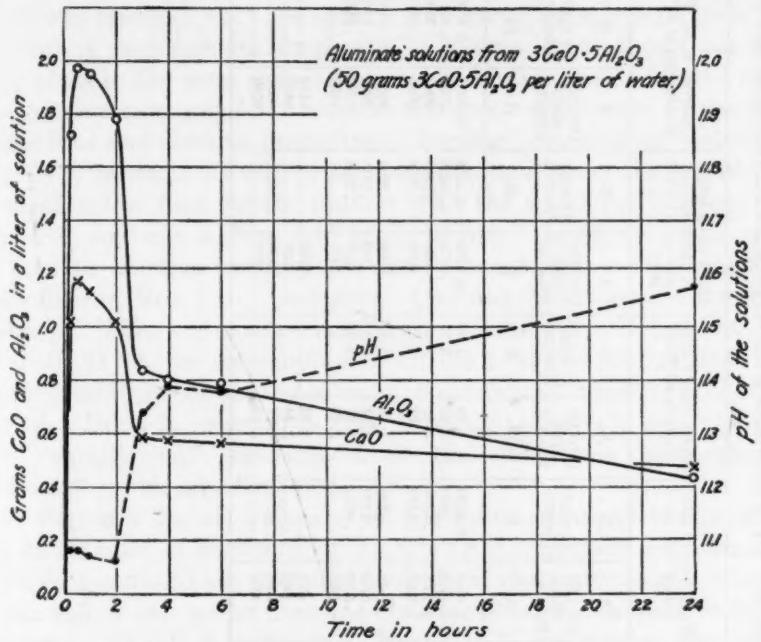

FIG. 5.—*Showing the composition and pH of aluminate solutions from $3CaO.5Al_2O_3$ as functions of the time of contact with water*

CaO per liter, respectively) are plotted against the time (in hours) of contact of the aluminate with water before filtering. The pH values of the solutions (column 13) are also plotted against this time.

From the data (columns 3 and 5 of Table 3, as plotted in Figure 5) it is apparent that the reaction of water on the 3:5 calcium aluminate progresses rapidly. The quantity of both lime and alumina dissolved by the water attained a maximum in 30 minutes and thereafter gradually decreased until two hours had elapsed. Between two and three hours there was a rapid decrease of alumina and lime in solution, and this rate of diminution, in turn, became less as time progressed. An apparent state of equilibrium was reached only after an elapse of several weeks.

TABLE 3.—*Composition and pH of aluminate solutions from 3:5 calcium aluminate ($3CaO.5Al_2O_3$)*

No.	Time of contact of $3CaO.5Al_2O_3$ with water before filtering	Total alumina in solution, g Al_2O_3 per l		Total lime in solution, g CaO per l		Molar ratio CaO/Al_2O_3 in solution		Lime in solution in excess of $CaO.Al_2O_3$, g CaO per l		Observed E. M. F. of solutions at 30°		pH of solutions at 30°		Ratio of lime in solution in excess $CaO.Al_2O_3$ $\frac{(CaO)_A}{(CaO)_B}$	Ratio of hydroxyl-ion concentration $\frac{[OH^-]_A}{[OH^-]_B}$
		A	B	A	B	A	B	A	B	A	B	A	B		
		Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	15 minutes	1.7230	0.2015	1.0240	0.4370	1.08	3.94	0.0763	0.3268	0.9097	0.9501	11.08	11.75	0.233	0.213
2	30 minutes	1.9725	.1875	1.1725	.3890	1.07	3.77	.0876	.2859	.9097	.9450	11.08	11.67	.306	.259
3	1 hour	1.9520	.1720	1.1360	.3750	1.05	3.90	.0624	.2804	.9093	.9493	11.07	11.74	.222	.216
4	2 hours	1.7710	.2095	1.0210	.4250	1.05	3.69	.0669	.3098	.9085	.9485	11.06	11.72	.216	.216
5	3 hours	.8350	.2865	.5855	.4370	1.28	2.77	.1252	.2794	.9254	.9458	11.34	11.68	.447	.457
6	4 hours	.8020	.2700	.5760	.4400	1.31	2.96	.1350	.2915	.9283	.9465	11.39	11.69	.463	.494
7	6 hours	.7875	.2720	.5690	.4350	1.31	2.91	.1359	.2854	.9277	.9465	11.38	11.69	.476	.487
8	1 day	.4360		.4805		2.00		.2407		.9400		11.58			
9	3 days	.3245		.4525		2.53		.2740		.9419		11.61			
10	7 days	.2475		.4670		3.44		.3309		.9485		11.72			
11	14 days	.2030		.4655		4.17		.3538		.9502		11.75			
12	407 days	.1505		.4300		5.19		.3473		.9500		11.75			

The 3:5 calcium aluminate is less basic than the monocalcium aluminate, $CaO.Al_2O_3$. However, both of these anhydrous calcium aluminates reacted with water in the early periods to form calcium aluminate solutions with a molar ratio, CaO/Al_2O_3, of approximately 1. This indicates that the lime and alumina are dissolved by the water as the calcium salt of monobasic aluminic acid. A more complete discussion of this relation will be presented later in this paper.

At the later periods (Table 3, Nos. 8 to 12, inclusive) the molar ratio of lime to alumina in solution (column 7) increased, with a simultaneous increase in the pH (column 13), until once more the point pH 11.75 was reached, as in the case of corresponding solutions from the anhydrous monocalcium aluminate. Changes identical to these also took place in the more or less metastable solutions when filtered from the reaction mixture of 3:5 calcium aluminate and water. A portion of the lime and alumina precipitated, leaving "equilibrium" solutions (Table 3, columns B) similar to those obtained when the anhydrous aluminate had been left in contact with the water for long periods (Table 3, columns A, Nos. 9 to 12, inclusive). Again the molar ratio of lime to alumina increased, as can be noted from a comparison of the values of Nos. 1 to 7, inclusive, of column 7 to those of column 8, Table 3. This was accompanied by an increase in pH (column 14) to about 11.75, the value obtained for the solutions filtered from the reaction mixtures of the water and 3:5 calcium aluminate at the later periods (Table 3, column 13, Nos. 9 to 12, inclusive), and also for the "equilibrium" solutions from the anhydrous monocalcium aluminate previously discussed.

In Figure 6 the pH values of all the solutions are plotted against the molar ratio of lime to alumina, CaO/Al_2O_3, in these solutions.

Table 4 contains the chemical analyses of the material precipitated at the end of two weeks from the clear metastable calcium aluminate solutions. (Table 3, columns A, Nos. 1 to 7, inclusive.) Precipitation of this material was initiated in the more concentrated solutions (Nos. 1 to 4, inclusive) within two or three hours after filtering. The small spherulites did not appear until two or three days later. On the other hand, the more dilute solutions (Nos. 5 to 7, inclusive) remained clear for a day or two, following which small spherulites were observed on the walls of the flasks. Later these crystals were covered with a thin film of amorphous material. Chemical analyses and petrographic examinations of the material precipitated from the metastable solutions indicated that hydrated alumina and hydrated tricalcium aluminate were precipitated as equilibrium was approached. Except for a small quantity of calcite in three of the samples, no other phases were observed. The refractive index of the amorphous material in sample No. 2 was approximately 1.55. The index, ω, of

the hexagonal plates in samples Nos. 5, 6, and 7 varied between 1.522 and 1.532. These variations may be due to the degree of drying and presence of some water between the laminæ of the crystals. It does not, however, prove the presence of a new compound.

TABLE 4.—*Chemical analyses of the material precipitated from the clear metastable calcium aluminate solutions prepared by shaking anhydrous 3 : 5 calcium aluminate with water in the proportion of 50 g $3CaO.5Al_2O_3$ per liter of water*

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Time of contact of aluminate with water	15 min.	30 min.	1 hr.	2 hrs.	3 hrs.	4 hrs.	6 hrs.
Analysis of precipitate:							
Per cent CaO	16.08	17.14	17.20	15.70	13.62	(1)	(1)
Per cent Al_2O_3	44.50	41.68	41.70	45.44	50.02	(1)	(1)
Per cent H_2O	39.72	41.17	42.17	38.23	36.98	(1)	(1)
Total	100.30	99.99	101.07	99.37	100.62	.....	.....
Molar ratio CaO/Al_2O_3 in the precipitate from above analyses	0.642	0.747	0.749	0.626	0.495	.....	.....
Molar ratio CaO/Al_2O_3 in the precipitate computed from analyses of solutions before and after precipitation	.700	.808	.777	.689	.483	0.465	0.452

[1] Too small amount for analysis.

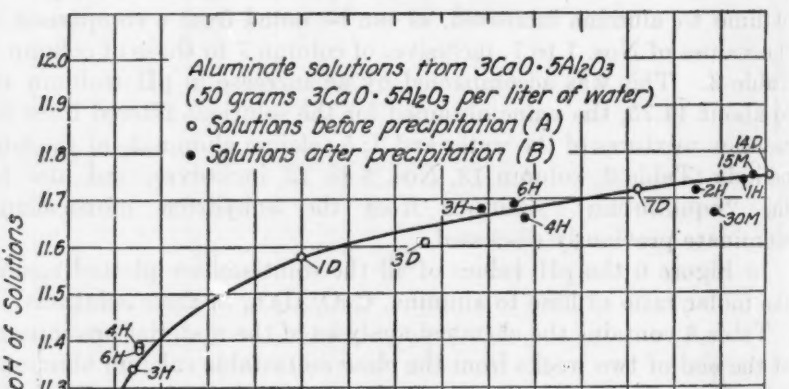

FIG. 6.—*Showing the pH of aluminate solutions from $3CaO.5Al_2O_3$ as a function of the molar ratio CaO/Al_2O_3 in solution*

It is seen, therefore, that the reaction of water with 3:5 calcium aluminate is analogous to its reaction with monocalcium aluminate

previously described in more detail. In the early periods of the reaction, metastable calcium aluminate solutions are formed which have a molar ratio, CaO/Al_2O_3, approximately 1. After these solutions are filtered from the reaction mixtures they subsequently decompose on standing, with an attendant precipitation of a portion of the alumina and lime as hydrated alumina and hydrated tricalcium aluminate. The resulting solutions, which are in equilibrium with these two solid phases, attain the same composition as the solutions obtained by filtering the mixtures of water and either of the anhydrous aluminates after several weeks have elapsed. In all cases the pH values of the solutions at the later periods are higher than those of the corresponding metastable solutions obtained directly upon filtering from the reaction mixtures. The molar ratio of lime to alumina in the solutions obtained at the later periods is also higher.

6. REACTION OF WATER ON THE 5:3 CALCIUM ALUMINATE ($5CaO.3Al_2O_3$)

The procedure for the study of the reaction of water on the 5:3 calcium aluminate, $5CaO.3Al_2O_3$, was the same as that adopted in the investigation of the mono and 3:5 calcium aluminates. Although the reaction mixtures of the 5:3 calcium aluminate and water were shaken vigorously to prevent setting, nevertheless, a portion of the material soon agglomerated in small lumps as a result of the formation of hydrated material on the outside of the individual grains, which had a tendency to cohere and prevent the further penetration of water. The mixtures of this aluminate and water did not filter as readily as those of either the mono or 3:5 calcium aluminate.

The composition and pH of the resulting aluminate solutions are recorded in Table 5 and represented diagramatically in Figure 7. It may be noted from columns 3 and 5 of Table 5, as plotted in Figure 7, that the total quantities of both alumina and lime dissolved by the water increased rapidly for 30 minutes, then more slowly, and finally reached a maximum at the end of two hours. This was followed by a rapid decrease, which, in turn, became less after six hours had elapsed. An apparent state of equilibrium was reached only after several weeks had elapsed. Also, the total quantities of alumina and lime dissolved by the water in the early periods were less than the corresponding quantities of these same materials taken into solution

TABLE 5.—*Composition and pH of aluminate solutions from 5:3 calcium aluminate ($5CaO.3Al_2O_3$)*

No.	Time of contact of $5CaO.3Al_2O_3$ with water before filtering	Total alumina in solution, g Al_2O_3 per l		Total lime in solution, g CaO per l		Molar ratio CaO/Al_2O_3 in solution		Lime in solution in excess of $CaO.Al_2O_3$ g CaO per l		Observed E. M. F. of solutions at 30°		pH of solutions at 30°		Ratio of lime in solution in excess $CaO.Al_2O_3$	Ratio of hydroxyl-ion concentration
		A	B	A	B	A	B	A	B	A	B	A	B		
		Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	$(CaO)_A$ / $(CaO)_B$	$[OH^-]_A$ / $[OH^-]_B$
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	15 minutes	1.0530	0.3215	0.7370	0.4575	1.27	2.58	0.1578	0.2808	0.9264	0.9431	11.36	11.63	0.562	0.528
2	30 minutes	1.2960	.2715	.8335	.4870	1.15	3.26	.1107	.3376	.9208	.9501	11.26	11.75	.328	.326
3	1 hour	1.3400	.2240	.8575	.5011	1.16	4.11	.1205	.3838	.9204	.9520	11.26	11.78	.314	.298
4	2 hours	1.3625	.3050	.8420	.4850	1.15	2.90	.0926	.3172	.9178	.9488	11.21	11.73	.292	.305
5	3 hours	.9855	.4025	.6705	.4770	1.23	2.15	.1285	.2556	.9240	.9405	11.32	11.59	.503	.531
6	4 hours	.9455	.3765	.6300	.4860	1.21	2.34	.1100	.2789	.9196	.9464	11.24	11.52	.394	.416
7	6 hours	.5960	.5925	.5195	.5000	1.58	1.58	.1917	.1741	.9398	.9370	11.52	11.53		
8	1 day	.4355		.4625		1.93		.2230		.9404		11.59			
9	3 days	.3425		.4380		2.31		.2496		.9458		11.68			
10	7 days	.3195		.4975		2.83		.3218		.9465		11.70			
11	14 days	.2940		.4900		3.03		.3283		.9499		11.75			
12	28 days	.2700		.4795		3.23		.3310		.9514		11.77			
13	385 days	.1725		.4910		5.18		.3961							

in the case of the other two aluminates (1:1 and 3:5, each of higher alumina content) previously studied. Nevertheless, the aluminate solutions formed during these periods had a molar ratio, CaO/Al_2O_3, of approximately 1, as can be seen from Table 5, column 7, Nos. 1 to 6, inclusive. This again indicates that initially the lime and alumina are dissolved as the calcium salt of monobasic aluminic acid. From these investigations it is apparent that, although monocalcium aluminate is dissolved as such, in each case, in the early

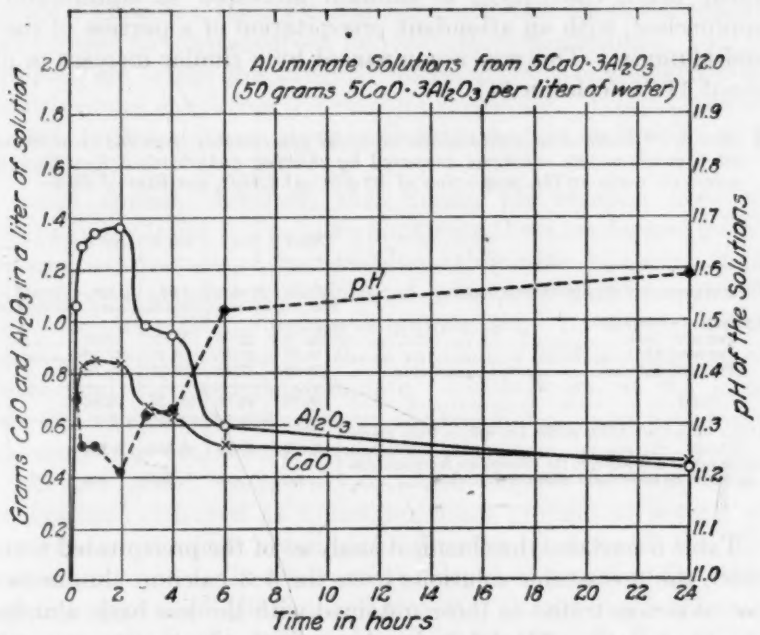

FIG. 7.—*Showing the composition and pH of aluminate solutions from $5CaO.3Al_2O_3$ as functions of the time of contact with water*

periods of the reaction, yet its total concentration, in grams per liter, is related to the chemical composition of the anhydrous aluminate from which it is formed. In the further study of the subsequent changes in the aluminate solutions, attended by increasing concentrations of calcium hydroxide, a more detailed discussion of the lower concentration of monocalcium aluminate in solution from the 5:3 calcium aluminate will be presented in this paper.

It is noted that at the later periods the molar ratio, CaO/Al_2O_3, in solution increased (Table 5, column 7), with a simultaneous increase

in the pH (Table 5, column 13), until the point pH 11.75 was reached. Lerch and Bogue [18] also have shown recently that the pH of equilibrium of 5:3 calcium aluminate and water is about 11.7, approximately this same value. *These values are also approximately those obtained when either the mono or the 3:5 calcium aluminate had been left in contact with water for long periods.*

Likewise, identical changes took place in the metastable solutions which were filtered from the reaction mixtures. On standing, the molar ratio, CaO/Al_2O_3, in solution increased as equilibrium was approached, with an attendant precipitation of a portion of the lime and alumina. This was accompanied by a similar increase in pH to about 11.75 (column 14).

TABLE 6.—*Chemical analyses of the material precipitated from the clear metastable calcium aluminate solutions prepared by shaking anhydrous 5:3 calcium aluminate with water in the proportion of 50 g $5CaO.3Al_2O_3$ per liter of water*

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Time of contact of aluminate with water	15 min.	30 min.	1 hr.	2 hrs.	3 hrs.	4 hrs.
Analysis of precipitate:						
Per cent CaO	15.78	12.96	10.78	12.44	.....	13.58
Per cent Al_2O_3	48.24	49.30	53.70	47.40	.....	48.90
Per cent H_2O	36.29	37.42	36.87	39.80	.....	37.71
Total	100.29	99.68	101.35	99.64	.....	100.19
Molar ratio CaO/Al_2O_3 in the precipitate from above analyses	0.593	0.477	0.365	0.480	.....	0.505
Molar ratio CaO/Al_2O_3 in the precipitate from analysis of solutions before and after precipitation	.604	.614	.625	.614	0.603	.460

Table 6 contains the chemical analyses of the precipitated material. Since the metastable solutions from the 5:3 calcium aluminate were not so concentrated as those obtained with the less basic aluminates, the precipitation was delayed. Accordingly, in growing more slowly the spherulites of tricalcium aluminate adhere more firmly to the walls of the flasks. Consequently, the resultant loss of this portion of the crystals firmly attached to the walls of the container might account for the lower molar ratio of lime to alumina in the precipitate, as calculated from the chemical analyses of the material recovered, in comparison to that computed from the analyses of the solutions before and after precipitation. Chemical analyses and petrographic examination of the material precipitated from the metastable solutions indicated that hydrated alumina and hydrated tricalcium aluminate were precipitated as equilibrium was approached. No calcite was found in any of the samples. The hexagonal plates, with

[18] J. Phys. Chem., **31**, p. 1627; 1927.

optical properties similar to those noted in previous aluminate precipitates, were present in all samples. The refractive index, ω, of these plates varied between 1.525 and 1.535. In samples Nos. 1, 4, and 6 the index of refraction of the amorphous isotropic material was approximately 1.48. In samples Nos. 2 and 3 it was nearly 1.55. Also, in samples Nos. 2, 3, and 4 a new phase in small amounts was noted. This consists of isotropic, isometric crystals with an index of refraction very close to 1.605. Incidentally, this index of refraction is about that of the isotropic crystals of the anhydrous 5:3 calcium aluminate. However, the crystals in the precipitated material appear as well-formed icositetrahedrons or rhombic dodecahedrons, and in this respect are unlike the irregular isotropic grains characteristic of the finely ground anhydrous 5:3 calcium aluminate. It is planned to investigate further this new phase, with the hope that its identity may be established.

It would appear, therefore, that during the reaction between water and anhydrous 5:3 calcium aluminate there are formed metastable and supersaturated monocalcium aluminate solutions from which hydrated alumina and hydrated tricalcium aluminate subsequently precipitate as equilibrium is approached. In these respects the reactions are analogous to those previously described in case of the mono and 3:5 calcium aluminate. Furthermore, at the later periods the solutions resulting from the reaction of water with these various anhydrous aluminates apparently approach the same equilibrium. A new phase, the identity of which has not yet been established, has been observed as a decomposition product of several of the metastable solutions obtained by filtering mixtures of the 5:3 aluminate and water. To what extent this phase, as well as the other two phases (hydrated alumina and hydrated tricalcium aluminate), may be present in the unfiltered mixture of the 5:3, 1:1, or 3:5 aluminates and water has not been determined.

7. REACTION OF WATER ON TRICALCIUM ALUMINATE ($3CaO.Al_2O_3$)

From his experiments on the time of set of the calcium aluminates, Bates[19] concludes that the mono and 3:5 calcium aluminates react with water much more slowly than the others high in lime. He found that by the use of about 10 per cent more water, in terms of cement, than is used in gauging Portland cement it is possible to knead thoroughly the 5:3 calcium aluminate without the appearance of any flash set. Initial set occurs in from 3 to 5 minutes after molding, and final set occurs in from 15 to 30 minutes, the latter

[19] B. S. Tech. Paper No. 197.

being accompanied by a marked evolution of heat. On the other hand, the addition of water to the tricalcium aluminate produces a very vigorous reaction, manifesting itself almost immediately by a rapid rise in temperature, until the mass steams vigorously and assumes a "flash set."

Notwithstanding, it was hoped that it would be possible to follow the changes in the composition of the solutions resulting from the reaction of water on the tricalcium aluminate in a manner similar to that used in the case of the other aluminates. However, the attempt was soon abandoned. When the finely powdered tricalcium aluminate was added to the water it quickly agglomerated into balls which hydrated on the exterior to hard masses which prevented the penetration of water to the interior; consequently, large masses of unhydrated material were present. Furthermore, the resulting mixture filtered very slowly, evidently due to the precipitation of material within the pores of the filter paper, since the clear filtrates, which were first obtained, became cloudy very quickly on standing. Thus, since the addition of water to freshly prepared tricalcium aluminate, $3CaO.Al_2O_3$, produces such a very vigorous reaction, the changes in the composition of the resulting solutions could not be followed. Previous investigations [20] have indicated that its setting is due to the formation of hydrated tricalcium aluminate without the formation of hydrated alumina. This hydrated material may result entirely or in part from the direct hydration of the anhydrous aluminate, or, by analogy to the reactions of the other aluminates, from the reaction of the excess of lime on a calcium aluminate formed in the very early period of setting.

8. REACTION OF WATER ON A HIGH ALUMINA CEMENT

Having studied the mechanism of the reaction of water on the calcium aluminates, a commercial brand of high alumina cement was investigated.

The chemical analysis [21] of this cement was:

	Per cent		Per cent
SiO_2	5.09	CaO	40.83
Fe_2O_3	10.92	MgO	0.81
Al_2O_3	38.98	Insoluble	2.83
TiO_2	1.90	Loss on ignition	1.51

The monocalcium aluminate ($CaO.Al_2O_3$) and the 3:5 calcium aluminate ($3CaO.5Al_2O_3$) are the chief constituents of high alumina cements of this composition, and the dicalcium silicate ($2CaO.SiO_2$) and iron compounds are the minor constituents.

In the study of the reaction of water on this cement the procedure was that followed in the investigation of the calcium aluminates.

[20] Klein and Phillips, B. S. Tech. Paper No. 43.

[21] Analysis by H. C. Stecker, of this bureau.

The aluminate solutions were obtained by shaking 250 g of cement with 5 liters of distilled water. The composition and pH of the solutions are recorded in Table 7 and represented diagramatically in Figure 8 from the data of columns 3, 5, and 13 of the table. The total quantities of both lime and alumina dissolved by the water increased for four hours, remained approximately constant for two more hours, and then decreased rapidly until about eight hours had elapsed, after which the decrease became less as time progressed. It was evident that a rapid precipitation of alumina and lime from solution occurred shortly after six hours, since the solutions above the cement became cloudy at this time. As in the reaction of the calcium aluminates, an apparent state of equilibrium was reached only after several weeks had elapsed. In general, the mechanism of the reaction of water on the high alumina cement was the same as with the mono, 3:5, and 5:3 calcium aluminates studied previously; that is, the formation of metastable solutions with lime and alumina in a molar ratio, CaO/Al_2O_3, of approximately 1, in the early periods of the reaction, followed by the precipitation of a portion of this lime and alumina as equilibrium is approached. In the same way the molar ratio of lime to alumina increased after this precipitation and was attended by an increase in the pH to about 11.70.

The chemical analyses of the materials precipitated, at the end of two weeks, from the clear metastable calcium aluminate solutions are recorded in Table 8. Precipitation of this material started from the more concentrated of these solutions (Table 7, columns A, Nos. 1 to 6, inclusive) within two or three hours after filtering. It was not until a day or two later that any precipitation was apparent in the more dilute solutions, Nos. 7 and 8, with the appearance of spherulites on the walls of the flasks. A day or two later these crystals were, in turn, covered with a thin film of amphorphous material. Microscopic examination revealed no phases other than those heretofore described. No calcite was found in any of the samples. The hexagonal plates, with optical properties similar to those noted previously, were observed in all samples. The isotropic and probably amorphous hydrated alumina had no perceptible birefringence, and a refractive index of about 1.570 ± 0.003. Although Gibbsite ($Al_2O_3.3H_2O$) is rather strongly birefringent and is undoubtedly crystalline, its mean refractive index, 1.573, agrees fairly well with the refractive index 1.570 ± 0.003 of the hydrated alumina. Also, in several of the samples, the isometric crystals with an index about 1.60 were found. These crystals appeared to be either icositetrahedrons or rhombic dodecahedrons and were similar to those observed previously in several samples from the 5:3 calcium aluminate. None of the samples showed any reaction with White's solution (used for the detection of free lime) after one hour of contact with this reagent.

TABLE 7.—*Composition and pH of aluminate solutions from high alumina cement*

No.	Time of contact of the cement with water before filtering	Total alumina in solution, g Al_2O_3 per 1		Total lime in solution, g CaO per 1		Molar ratio CaO/Al_2O_3 in solution		Lime in solution in excess of $CaO.Al_2O_3$ g CaO per 1		Observed E. M. F. of solutions at 30°		pH of solutions at 30°		Ratio of lime in solution in excess $CaO.Al_2O_3$ $\frac{(CaO)_A}{(CaO)_B}$	Ratio of hydroxyl-ion concentration $\frac{[OH^-]_A}{[OH^-]_B}$
		A	B	A	B	A	B	A	B	A	B	A	B		
		Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium	Directly upon filtering	At equilibrium		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	15 minutes	1.5400	0.2415	0.9720	0.4715	1.12	3.55	0.1250	0.3387	0.9193	0.9452	11.24	11.67	0.369	0.371
2	30 minutes	1.5210	.2325	.9790	.4675	1.17	3.66	.1424	.3396	.9188	.9447	11.23	11.66	.419	.371
3	1 hour	1.6785	.2255	1.0535	.4960	1.14	4.00	.1303	.3720	.9164	.9465	11.19	11.69	.350	.316
4	2 hours	1.8930	.2050	1.1500	.4360	1.10	3.87	.1089	.3200	.9166	.9448	11.19	11.66	.340	.339
5	4 hours	2.0175	.1940	1.2080	.3860	1.09	3.62	.0990	.2793	.9152	.9473	11.17	11.70	.354	.291
6	6 hours	2.0200	.2085	1.2040	.4255	1.08	3.70	.0930	.3108	.9138	.9477	11.15	11.71	.299	.271
7	8 hours	.9880	.2555	.6610	.4195	1.22	2.98	.1176	.2790	.9217	.9430	11.28	11.62	.421	.442
8	10 hours	.9015	.2810	.6115	.4100	1.23	2.65	.1158	.2554	.9225	.9399	11.29	11.58	.453	.512
9	1 day	.4410	----------	.4375	----------	1.80	----------	.1950	----------	.9338	----------	11.48	----------	----------	----------
10	3 days	.2315	----------	.3880	----------	3.03	----------	.2607	----------	.9446	----------	11.66	----------	----------	----------
11	7 days	.1585	----------	.3055	----------	3.55	----------	.2183	----------	.9437	----------	11.64	----------	----------	----------
12	14 days	.1900	----------	.3660	----------	3.50	----------	.2615	----------	.9453	----------	11.67	----------	----------	----------

TABLE 8.—*Chemical analyses of the material precipitated from the clear metastable calcium aluminate solutions prepared by shaking a high alumina cement with water, in the proportion of 50 g per liter of water*

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Time of contact of cement with water	15 min.	30 min.	1 hr.	2 hrs.	4 hrs.	6 hrs.	8 hrs.	10 hrs.
Analysis of precipitate:								
Per cent CaO	13.96	13.32	13.77	14.66	13.00	16.00	.....	.....
Per cent Al_2O_3	46.40	50.52	49.36	44.44	48.80	44.88	.....	.....
Per cent H_2O	39.39	36.61	35.54	41.15	37.95	39.40	.....	.....
Total	99.95	100.45	101.67	100.25	99.75	100.28	.....	.....
Molar ratio CaO/Al_2O_3 in the precipitate from the above analyses	0.547	0.463	0.507	0.600	0.484	0.632	.....	.....
Molar ratio CaO/Al_2O_3 in the precipitate computed from analyses of solutions before and after precipitation	.709	.722	.700	.768	.819	.781	0.694	0.590

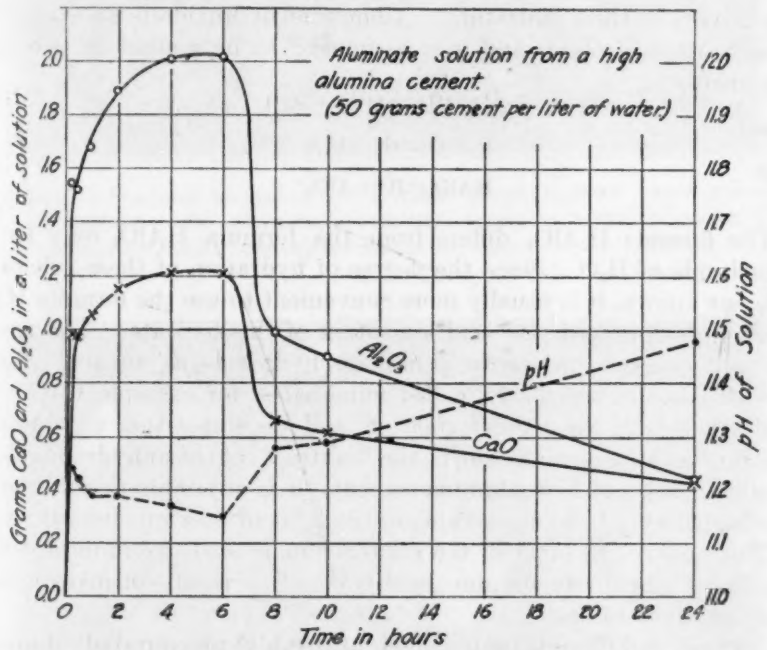

FIG. 8.—*Showing the composition and pH of aluminate solutions from a high alumina cement as functions of the time of contact with water*

A microscopic examination of the fractured surfaces of some briquettes of high alumina cement which had been stored in water for a year revealed in some small cavities hexagonal plates with optical properties similar to those noted previously. Several of these crystals are seen in Figures 9 to 12, inclusive.

The reaction of the iron in the cement has not been determined. The constituents containing iron and silica apparently influence the

rate of the setting of the aluminates. However, no iron was detected in any of the aluminate solutions.

From these experiments it would appear that the reactions between water and the high alumina cement, as well as the monocalcium aluminate, the 3:5 calcium aluminate, and the 5:3 calcium aluminate, were in part related to the precipitation of hydrated alumina and crystalline hydrated tricalcium aluminate from metastable and supersaturated monocalcium aluminate solutions. It is hoped that the following consideration of the constitution of the aluminate solutions will throw further light upon the formation and decomposition of the metastable monocalcium aluminate solutions.

9. CONSTITUTION OF THE ALUMINATE SOLUTIONS

Amphoteric electrolytes give both hydrogen and hydroxyl ions as products of their ionization. Aluminum hydroxide is an example of such an electrolyte, and it is assumed [22] to be ionized in two ways, namely,

$$Al(OH)_3 \rightleftharpoons Al^{+++} + 3OH^-$$

and

$$H_3AlO_3 \rightleftharpoons H^+ + H_2AlO_3^-$$

or

$$HAlO_2 \rightleftharpoons H^+ + AlO_2^-$$

The formula H_3AlO_3 differs from the formula $HAlO_2$ only by one molecule of H_2O. Since the degree of hydration of these substances is not known, it is usually more convenient to use the formula $HAlO_2$ when dealing with the acid ionization of this hydrate. The present study concerns primarily aluminum hydroxide as an acid wherein with bases it forms salts called aluminates (for example, $Ca(AlO_2)_2$). Furthermore, since the formation and decomposition of aluminate solutions apparently occur in the "setting" of the anhydrous calcium aluminates and high alumina cements, it is advisable to consider the constitution of the aluminates in the light of previous investigations. The evidence in favor of the existence in aqueous solution of definite salts of monobasic aluminic acid is based on results of investigations along several lines.

Prescott [23] found that 1 mol of freshly precipitated aluminum hydroxide dissolves in exactly 1 mol of sodium or potassium hydroxide and maintained, therefore, that the solution must contain the monoaluminate (for example, the meta-aluminate). The same formula for the alkali aluminate was set forth by Cavazzi,[24] who found, by the addition of metallic aluminum to the alkalis, that 1 mol Al went into solution for each mol of NaOH or KOH. The same combination (1 alkali for 1 Al) was also found by Bogussky

[22] E. W. Washburn, Principles of Physical Chemistry, p. 362; 1921; McGraw-Hill Book Co., New York.
[23] J. Am. Chem. Soc., **2**, p. 27; 1880; Chem. News, **42**, p. 29; 1880.
[24] Gazz. chim. ital., **15**, p. 205; 1885.

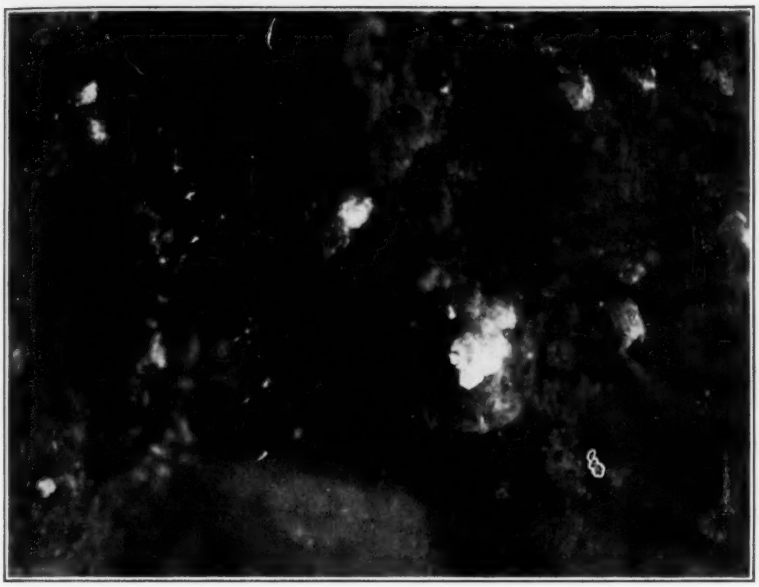

FIG. 9.—*Fractured surface of neat briquette of high alumina cement stored in water for one year, showing cavities containing hexagonal plates of colorless hydrated tricalcium aluminate.* (×40.)

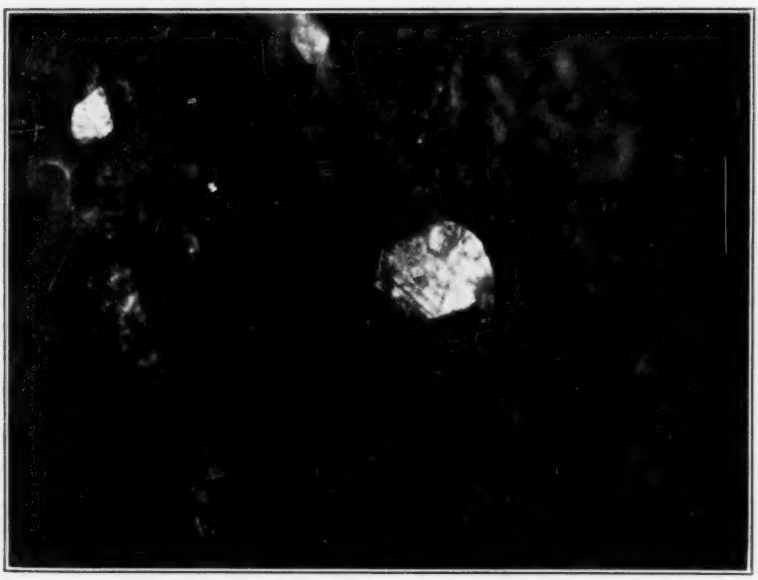

FIG. 10.—*A flat hexagonal plate of hydrated tricalcium aluminate removed from a cavity for photographing.* (×40.)

FIG. 11.—*Fractured surface of neat briquette of high alumina cement stored in water for one year, showing cavities containing hexagonal plates of hydrated tricalcium aluminate.* (×50.)

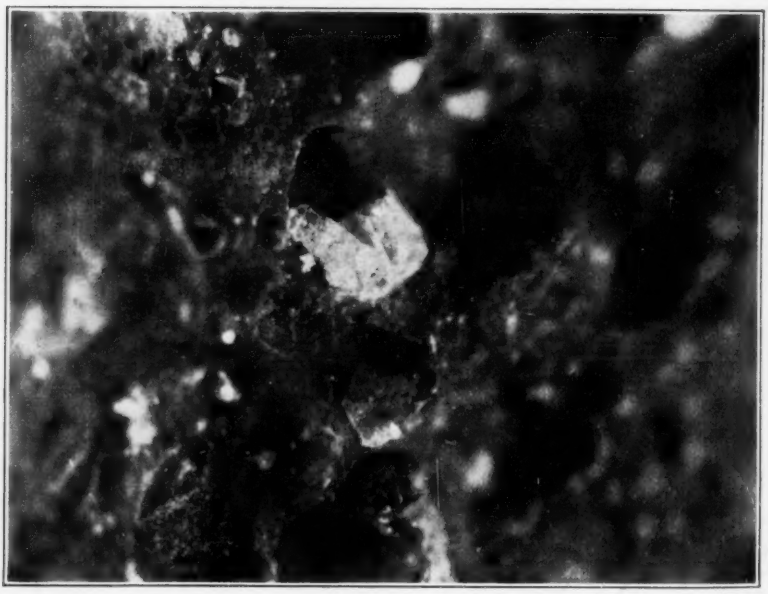

FIG. 12.—*Same as Figure 11, but oriented.* (×40.)

and Zaljesky,[25] as well as by Lyte.[26] Observations [27] on this subject were also made by H. St. C. Deville, A. Ditte, F. Russ, and A. Glässner. Numerous investigators have shown that gelatinous aluminum hydroxide, on standing, changes over to a new form which is often referred to as a crystalline variety and which is difficultly soluble, even in an excess of alkali. This change is known as the "aging" process. Therefore, the solubility ratio is only applicable for deducing a formula for the salt in solution when the freshly precipitated hydroxide is used. Herz [28] found that although freshly precipitated aluminum hydroxide dissolves in alkali to form the meta-aluminate, $NaAlO_2$, yet, if alumina is dried, an ortho-aluminate of the composition, Na_3AlO_3, is apparently formed. However, there seems to be no evidence for assuming that the latter solution contains the ortho-aluminate, as Slade [29] found that the ratio of alkali to alumina in the solubility determinations may range from 2 to 1 to 10 to 1, according to the condition of precipitation and the duration and mode of drying of the alumina. Wood's [30] solubility determinations of aluminum and of aluminum hydroxide in solutions of sodium hydroxide, after allowing for a slight excess of alkali over the amount required to form monosodium aluminate owing to partial hydrolysis of the salt, agree with the assumption that sodium meta-aluminate, $NaAlO_2$, is formed, but not the ortho-salt, Na_3AlO_3. Carrara and Vespignani [31] conclude that, even in presence of a large excess of potassium hydroxide, aluminum hydroxide forms only potassium monoaluminate.

The constitution of aluminate solutions has also been investigated by the freezing-point method. Noyes and Whitney [32] dissolved aluminum sheet metal in both sodium and potassium alkali solutions (ranging from about 0.2 to 0.5 *N*) and found no difference between the freezing point of these solutions and those free from aluminum and so concluded that the formula of meta-aluminate was $XAlO_2$ (X = alkali). Slade [33] also concluded from freezing-point determinations that sodium aluminate in solution is the salt of monobasic aluminic acid. His observations were confirmed by Heyrovsky for sodium, ammonium,[34] and also for alkaline earth aluminates.[35]

[25] Chem. Zt., **14**, p. 148; 1890.
[26] Chem. News, **51**, pp. 109, 201; 1885.
[27] Deville, Ann. chim. phys., **61**, p. 333; 1861; Ditte, Compt. rend., **116**, pp. 183, 386; 1893; Russ, Z. anorg. Chem., **41**, p. 216; 1904; Glässner, Chem. Ind., **25**, p. 186; 1902.
[28] Z. anorg. Chem., **25**, p. 155; 1900.
[29] Z. Elektrochem., **17**, p. 261; 1911; cf. W. Herz, Z. Elektrochem., **17**, p. 403; 1911
[30] J. Chem. Soc. (London), **93**, p. 417; 1908.
[31] Gazz. chim. ital., **30**, pp. ii, 35; 1900.
[32] Z. physik. Chem., **15**, p. 694; 1894; Tech. Quart., **7**, p. 1; 1894.
[33] Z. Elektrochem., **17**, p. 261; 1911.
[34] J. Chem. Soc. (London), **117**, p. 1013; 1920.
[35] Chem. News, **125**, p. 198; 1922.

Conductance methods have also been used to determine the constitution of aluminate solutions. Carrara and Vespignani [36] found an appreciable decrease in the conductivity of potassium aluminate solutions as compared with the corresponding solutions of potassium hydroxide. Hantzsch [37] likewise found that solutions containing 1 Na for 1 Al, in the pure state, had a conductance lower than that of the corresponding solutions of sodium hydroxide. Upon the further addition of NaOH to a freshly prepared sodium aluminate solution, he discovered that the conductivity was additive, showing thereby that the additional alkali does not combine with the aluminate. This is further proof of the monobasic nature of the aluminic acid. He observed, also, that the monocalcium aluminate solutions were unstable and that aluminum hydroxide precipitated on standing. It will be recalled that aluminum hydroxide (hydrated alumina) was found to be one of the decomposition products of the metastable calcium aluminate solutions. Hantzsch considers the decomposition of the aluminate as resulting from its hydrolysis, proceeding in the following manner:

$$Al(OH_2)O^- + H_2O \leftrightarrows Al(OH_2).OH + OH^-$$

this being indicated by an increase in the conductivity. He found, however, that no visible deposition of hydrated alumina took place until the conductivity had increased considerably. Hantzsch believed this indicated that the aluminum hydroxide became colloidal prior to such deposition. Further conductivity measurements on dilute sodium aluminate solutions were made by Slade and Polack.[38] The solutions were obtained by saturation of sodium hydroxide with metallic aluminum, being guided by the volume of H_2 evolved in securing an atomic ratio of Na:Al in the solution as nearly 1:1 as possible. From their experiments they conclude that there is no evidence of the existence of colloidal aluminum hydroxide in the sodium aluminate solutions, as was supposed by Hantzsch, and that whenever hydrolysis takes place crystalline aluminum hydroxide is deposited. They also conclude that their examination of sodium aluminate solutions in the ultramicroscope gave no definite evidence of the existence or nonexistence of colloidal particles. Heyrovsky [39] also made a study of the conductance of aluminate solutions, prepared by adding metallic aluminum to dilute solutions of sodium hydroxide. He showed that the conductance falls regularly with increasing concentration of the aluminate. The slope of the equivalent conductance curve remains constant when the ratio of the gram-atoms Na:Al is either 3:1 or 2:1, indicating that no formation of a salt of tri or di basic

[36] Gazz. chim. ital., **30**, pp. ii, 35; 1900.
[37] Z. anorg. Chem., **30**, p. 280; 1902.
[38] Trans. Faraday Soc., **10**, p. 150; 1914.
[39] J. Chem. Soc. (London), **117**, p. 1013; 1920.

aluminic acid takes place. When, however, the ratio becomes 1:1, spontaneous decomposition of the solution occurs, during which crystalline aluminum hydroxide separates out, and the conductance resultantly increases in the manner described by Slade and Polack. Heyrovsky [40] also showed that the decrease in conductivity of barium hydroxide upon the addition of metallic aluminum is quite regular and linear until the atomic ratio Ba:Al in solution becomes 1:2. These experiments indicate that no ions other than monovalent anions substitute for the hydroxyl ions in neutralization.

Electromotive force measurements have also been employed in establishing the constitution of the aluminate solutions. Thus, Hildebrand [41] and Blum [42] have measured the change in hydrogen-ion concentration as sodium hydroxide or potassium hydroxide is progressively added to a solution of aluminum chloride until the aluminum hydroxide is precipitated and subsequently dissolved. The points of inflection in the precipitation curves, as obtained by Blum, confirm the observations of Prescott that 1 mol of freshly precipitated aluminum hydroxide dissolves in exactly 1 mol of an aqueous solution of sodium and potassium hydroxide and indicates, therefore, the existence of definite aluminates of the formulas $NaAlO_2$ and $KAlO_2$, or multiples thereof. Blum found the points of inflection when the aluminum hydroxide was dissolved by sodium and potassium hydroxide to be at pH values of approximately 10.5 and 11.0, respectively. Britton [43] has investigated the constitution of the soluble aluminates of calcium, barium, and strontium. In each of his titrations the precipitated aluminum hydroxide redissolved completely when approximately another equivalent of alkaline earth hydroxide was added, the redissolving being indicated by the characteristic inflections of the titration curves. The points of inflection in the titration of aluminum chloride with barium and strontium hydroxides were at pH values of 10.43 and 10.60, respectively, and in the titration of aluminum sulphate with calcium hydroxide at pH, 10.17.

Hence, the bulk of the evidence (as based on the solubility ratio, the freezing point, conductivity, and electromotive force measurements) indicates that the alkali and alkaline earth aluminates exist in aqueous solution as salts of monobasic aluminic acid.

Nevertheless, Mahin and his coworkers [44] have concluded from their observations of the aluminate solutions that the aluminates do not exist in solution as definite salts, but that the solubility of aluminum hydroxide in bases is due principally to its colloidal properties. Their conclusions have been severely criticized by Blum and

[40] Chem. News, **125**, p. 198; 1922.
[41] J. Am. Chem. Soc., **35**, p. 864; 1913.
[42] J. Am. Chem. Soc., **35**, p. 1499; 1913.
[43] J. Chem. Soc., (London), p. 422; 1927.
[44] J. Am. Chem. Soc., **35**, p. 36; 1913.

by Slade and Polack. For details, one must consult the original articles.[45] Chatterji and Dhar [46] observed no appreciable changes in the conductivity of solutions of sodium hydroxide to which alumina was added and, hence, conclude that such solutions are instances of peptization and not of chemical combination. Weiser [47] has pointed out that the observations of Chatterji and Dhar merely indicate the failure of their experimental method to detect any change in conductivity in the highly alkaline solutions, rather than the absence of a change.

Therefore, it may be said that the constitution of the aluminates in aqueous solution is apparently well established. The work described in this paper adds to the evidence in favor of the existence in solution of a salt of monobasic aluminic acid. It has been shown that a high alumina cement and the anhydrous calcium aluminates, differing so widely in chemical composition, reacted with the water in the early periods of setting to form calcium aluminate solutions with a molar ratio, CaO/Al_2O_3, in each case close to 1.

It has been shown by previous investigators that the aluminate solutions are metastable and that, on standing, hydrated alumina precipitates. Also, from the present study it is apparent that the instability of the calcium aluminate solutions is closely related to the reaction of both anhydrous calcium aluminates and high alumina cements due to the precipitation not only of hydrated alumina but also of hydrated tricalcium aluminate. The precipitation of alumina from the aluminate solutions is accompanied by an increase in pH. Johnston [48] accounts for the abnormal alkalinity of the alkali aluminates by the progressive hydrolysis which takes place owing to the slight solubility of the aluminic acid, which first separates in the gelatinous or colloidal and later in the less soluble crystalloidal form. Bayer [49] and Ditte [50] have likewise assumed that two forms of hydrated alumina (aluminic acid) are involved—the gelatinous and the crystalline. A solution which is saturated with the gelatinous aluminic acid must, therefore, be supersaturated with respect to the crystalline form, which is less soluble. Fricke [51] has made an extensive study of the hydrolysis of the alkali aluminates and has found that the intensity of "aging" is directly proportional to the hydroxyl-ion concentration. He [52] and other investigators,[53] by means of X-ray diffraction patterns, have shown that this aged alumina is crystalline. A saturated mono-

[45] Blum, J. Am. Chem. Soc., **36**, p. 2383; 1914; cf. **35**, p. 1499; 1913; Slade and Polack, Trans. Faraday Soc., **10**, p. 150; 1914; Mahin, J. Am. Chem. Soc., **36**, p. 2381; 1914; cf. **35**, p. 36; 1913.
[46] Chem. News, **121**, p. 253; 1920.
[47] H. B. Weiser, Hydrous Oxides, p. 117; 1926; McGraw-Hill Book Co., New York.
[48] Private communication to Blum; J. Am. Chem. Soc., **35**, p. 1503; 1913.
[49] Bayer, Chem. Ztg., **12**, p. 1209; 1889.
[50] Ditte, Compt. rend., **116**, pp. 183, 386, 509; 1893.
[51] Z. Elektrochem., **26**, p. 129; 1920.
[52] Fricke and Weaver, Z. anorg. allgem. Chem., **136**, p. 321; 1924.
[53] Böhm and Niclassen, Z. anorg. Chem., **132**, p. 1; 1924.

calcium aluminate solution is, therefore, even more unstable, since it is also supersaturated with respect to the tricalcium aluminate hydrate which crystallizes from solution together with the hydrated alumina. This indicates that there must be some ortho-aluminic acid in solution. However, it is very probable that the ionization constant of tribasic aluminic acid is so small in comparison with that of the monobasic aluminic acid that the aluminate solutions behave as the salt of the latter.

The experimental work of others supports the theory that aluminic acid in dilute solutions behaves primarily as a monobasic acid. In this investigation the relation of the pH of the calcium aluminate solutions to their chemical composition is in good agreement with this theory, as is evident from the following consideration:

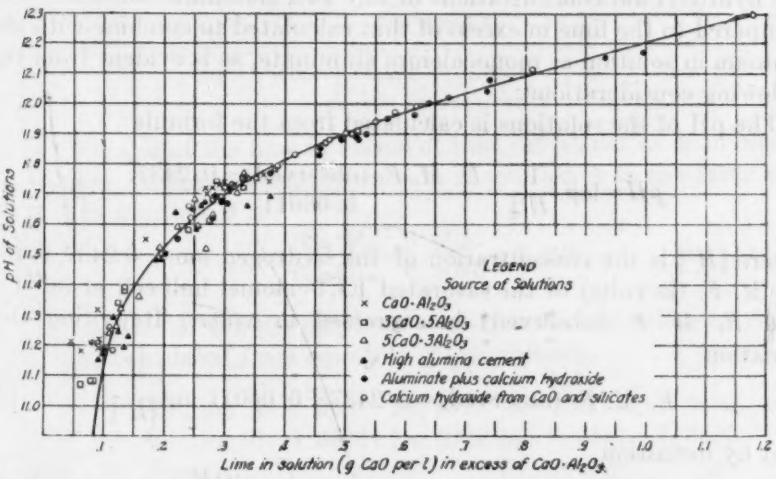

FIG. 13.—*Showing the pH of solutions as a function of the lime in solution (g CaO per liter) in excess of that calculated to combine with the alumina as* $CaO.Al_2O_3$

In this consideration the tacit assumption has been made that all the alumina in solution is combined with the lime as a monocalcium aluminate, and that any additional lime exists in solution as calcium hydroxide. It is also further assumed that the conclusions of Slade, Blum, and Heyrovsky that aluminic acid behaves as a fairly strong monobasic acid are correct. The question of the strength of this acid will be discussed later. On the basis of these assumptions, the pH values of all the aluminate solutions are plotted (fig. 13) against the lime (expressed as grams CaO per liter) in excess of that calculated to combine with the alumina as $CaO.Al_2O_3$. The data for these values are recorded in columns 9 and 10 of Tables 1, 3, 5, and 7. For comparison, some pH values of several pure calcium hydroxide solutions (also expressed as grams CaO per liter) are likewise plotted in

Figure 13. It can be seen from this figure that, in general, the two sets of values fall upon the same curve. The greatest deviations from the curve are those values representing the aluminate solutions which contain the higher concentration of monocalcium aluminate with the corresponding smaller concentration of "free" calcium hydroxide. In such solutions the hydrolysis of the monocalcium aluminate is a more important factor in establishing the resulting pH than it is in those solutions containing less monocalcium aluminate and relatively more of "free" calcium hydroxide.

However, the increase in pH is always attended by an increase of the lime in solution that is in excess of the amount calculated to be in combination with the alumina in solution as monocalcium aluminate. This very close relationship was brought out more clearly when the hydroxyl-ion concentrations of any two aluminate solutions were compared to the lime in excess of that calculated to combine with the alumina in solution as monocalcium aluminate, as is evident from the following considerations:

The pH of the solutions is calculated from the formula:

$$pH = \log \frac{1}{[H^+]} = \frac{E.\ M.\ F.\ (\text{observed}) - 0.2437}{0.06011} \tag{1}$$

where $[H^+]$ is the concentration of the hydrogen ions; 0.2437 is the *E. M. F.* (in volts) of the saturated KCl-calomel half cell at 30° C.; and *E. M. F.* (observed) is expressed in volts. Rewriting this equation,

$$E.\ M.\ F.\ (\text{observed}) = 0.2437 + 0.06011 \log \frac{1}{[H^+]} \tag{2}$$

But by definition

$$Kw = [H^+]\,[OH^-] = 10^{-14} \text{ or } \frac{1}{[H^+]} = \frac{[OH^-]}{10^{-14}} \tag{3}$$

Combining equations (2) and (3),

$$E.\ M.\ F.\ (\text{observed}) = 0.2437 + 0.06011 \log \frac{[OH^-]}{10^{-14}} \tag{4}$$

or

$$E.\ M.\ F.\ (\text{observed}) = 0.2437 + 0.06011 \log [OH^-] + 0.8415 \tag{5}$$

which may be finally written as,

$$0.06011 \log [OH^-] = E.\ M.\ F.\ (\text{observed}) - 1.0852 \tag{6}$$

Equation (6) may, therefore, be used to calculate the ratio of the hydroxyl-ion concentrations of any two solutions. The numerical values of this ratio have been found to be, in general, in very good agreement with the ratio of the lime, in the same aluminate solutions, in excess of that calculated to combine with the alumina as a monocalcium aluminate of the formula, $CaO.Al_2O_3$.

As an example of such calculations the following is presented: Two aluminate solutions are hereby designated as solutions A and B, and the necessary data concerning these solutions are to be found in Table 1, as solutions No. 1, under columns A and B. For convenience, the data are repeated in the following table, which also contains the calculated values of the third column:

SOLUTION A

Total alumina in solution as g Al_2O_3 per l	Total lime in solution as g CaO per l	Lime as g CaO per l calculated to form $CaO.Al_2O_3$	Lime in solution in excess of $CaO.Al_2O_3$ (g CaO per l)	E. M. F. (observed) at 30° C.	pH at 30° C.
2.1850	1.2930	1.2018	0.0912	0.9165	11.19

SOLUTION B

0.2500	0.4455	0.1375	0.3080	0.9481	11.72

The ratio of the lime in excess of that calculated as combined with alumina as monocalcium aluminate in solution A to the same kind of lime in solution B is

$$\frac{(CaO)_A}{(CaO)_B}=\frac{0.0912}{0.3080}=0.296$$

The ratio of the hydroxyl-ion concentrations of solutions A and B can be calculated from equation (6), as follows:

$$\text{Solution A. } 0.06011 \log [OH^-]_A = 0.9165 - 1.0852$$
$$\text{Solution B. } 0.06011 \log [OH^-]_B = 0.9481 - 1.0852$$

Subtracting,

$$0.06011 \log \frac{[OH^-]_A}{[OH^-]_B} = -0.0316 \text{ or } \log \frac{[OH^-]_A}{[OH^-]_B} = -0.5240$$

From which it follows that the ratio,

$$\frac{[OH^-]_A}{[OH^-]_B}=0.300$$

In the same manner the ratio of lime in the aluminate solutions in excess of monocalcium aluminate, as given in columns 9 and 10 of Tables 1, 3, 5, and 7, is calculated and recorded in column 15 of these tables. Column 16 of the same tables contains the calculated ratio of the hydroxyl-ion concentrations of the corresponding solutions. These ratios indicate, in general, that the difference in pH of two aluminate solutions is closely related to the difference in the quantity of the lime in these solutions that is in excess of the amount calculated

as that combined with the alumina in the same solutions as a calcium salt of monobasic aluminic acid. It is realized that this is not an exact relation, as the hydrolysis of the monocalcium aluminate is a factor of moment. However, the above relation would not hold as well as it does unless meta-aluminic acid were a fairly strong monobasic acid. This work, therefore, is in agreement with the conclusions of Slade, Blum, and Heyrovsky that aluminic acid is a relatively strong monobasic acid. This, then, again presents the question as to the actual strength of this acid.

Slade[54] has concluded that monobasic aluminic acid has an ionization constant of at least 10^{-10}, which is about the same order of magnitude as that of boric acid. Assuming a saturated solution of crystalline aluminum hydroxide as containing 1 mg per liter, he calculated the concentration of the undissociated aluminic acid ($HAlO_2$), in neutral or alkaline solutions, as approximately 10^{-5}. The ionization constant, K_A, was then calculated from the equation

$$K_A [HAlO_2] = [H^+] [AlO_2^-] = 10^{-15}$$

giving the value

$$K_A = \frac{10^{-15}}{10^{-5}} = 10^{-10}$$

On the other hand, Blum[55] found an ionization constant, $K_A = [H^+] [AlO_2^-]/[HAlO_2]$, to be $10^{-8.3}$. The fact that this value is greater than that calculated by Slade is to be expected, since values of Slade were derived from solutions in equilibrium with the crystalline form of aluminum hydroxide, while those of Blum were obtained from solutions which were in equilibrium with the more soluble form of aluminum hydroxide. Even though these values might not be exact ones, they do show that aluminic acid is not a very weak monobasic acid. According to Heyrovsky,[56] aluminum hydroxide does not neutralize a base as does an acid, by furnishing hydrogen ions, but does so rather by the removal of hydroxyl ions to form complex anions, $Al(OH)_3 + OH^- = Al(OH)_4^-$. This is analogous to the behavior of compounds dissolved in an excess of reagents, for example, $Ag(CN)_2^-$, $HgI_4^=$, etc. Heyrovsky shows, however, that in dilute solutions only monovalent ions exist, and that aluminic acid is for all practical purposes considered to be monobasic. He concludes that the acidity of aluminum hydroxide is greater than may be apparent from ordinary analytical data, and that the alkaline solutions show the highest degree of neutralization in which aluminum hydroxide reacts in the "nascent state." The solutions of aluminate result, which, in the absence of carbon dioxide, at room temperature and decinormal dilution are not more than 1.5 per cent hydrolyzed.

[54] Z. anorg. Chem., **77**, p. 457; 1912.
[55] J. Am. Chem. Soc., **35**, p. 1499; 1913.
[56] J. Chem. Soc. (London), **117**, p. 1013; 1920; Chem. News, **125**, p. 198; 1922.

The difficulty of obtaining an exact value for the ionization constant of aluminic acid is obvious a priori, from merely a consideration of the properties of this acid. However, the value, $K_A = 1 \times 10^{-9}$, has been assumed as being approximately correct for the purpose of calculating the degree of hydrolysis, h, which is defined as that fraction of the total monocalcium aluminate in solution which has immediately undergone hydrolysis. The following calculations have been made to determine the approximate degree of hydrolysis and the resulting pH of a monocalcium aluminate solution (as solution A in the above table) which contained 2.1850 and 1.2930 g Al_2O_3 and CaO per liter, respectively, and with no free lime in excess of this amount. The degree of hydrolysis, h, can be calculated from the following approximation:[57]

$$\frac{h^2 C_S}{1-h} = \frac{K_W}{K_A} = K_H$$

C_S is the total concentration, in mols per liter, of the dissolved $CaO.Al_2O_3$; K_W is the ionization constant of water, 1×10^{-14}; and K_H is the hydrolysis constant of the aluminic acid. This equation is approximate, since there is involved the assumption that the degree of ionization of the strong base, $Ca(OH)_2$, in solution is numerically the same as the degree of ionization of the unhydrolyzed salt, $CaO.Al_2O_3$, in solution.

Substituting the above data and the calculated value for C_s

$$\frac{h^2(0.02143)}{1-h} = \frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 0.00001$$

Hence, $h = 0.0108$, or, the per cent hydrolysis $= 1.1$, approximately, which is in good agreement with the value, < 1.5, determined by Heyrovsky. This means that $0.02143 \times 0.011 = 0.000236$ mols, or 0.000472, equivalent of $Ca(OH)_2$, results from the initial hydrolysis of the monocalcium aluminate. To express this quantity of $Ca(OH)_2$ in terms of pH it is necessary to know its degree of ionization into Ca^{++} and OH^- in the presence of the ions of the unhydrolyzed monocalcium aluminate. While the degree of ionization is not known yet, some other calculations, based on the pH measurements, have indicated that the calcium hydroxide behaves as though it were about 60 per cent ionized in the presence of the above quantity of monocalcium aluminate. Accordingly, with an assumed ionization of 60 per cent, the pH of the hydrolyzed calcium aluminate solution has been calculated as follows:

$$pH = \log \frac{1}{[H^+]} = \log \frac{[OH^-]}{1 \times 10^{-14}} =$$
$$\log (0.000472 \times 0.6) + \log 10^{14} =$$
$$\log (0.0002832) + 14 = -3.55 + 14 = 10.45$$

[57] E. W. Washburn, Principles of Physical Chemistry, p. 369; 1921; McGraw-Hill Book Co., New York, N. Y.

Referring again to the electrometric titration curves obtained previously by Blum and by Britton, this value, pH = 10.45, is of the same order of magnitude as their pH values at the points of inflection in their curves wherein aluminum salts were titrated with alkali and alkaline earth hydroxides. These inflections mark the points at which aluminum hydroxide is completely redissolved with the formation of the monoaluminates.

It should be emphasized that the calculations submitted in this report give only approximate values. However, the values are approximately the same as those obtained by others and in this respect are in agreement with the assumptions that definite salts of monobasic aluminic acid exist in aqueous solution and that aluminic acid behaves as a relatively strong monobasic acid.

III. REACTION OF CALCIUM HYDROXIDE AND CALCIUM SILICATES ON CALCIUM ALUMINATE SOLUTIONS

1. REACTION OF CALCIUM HYDROXIDE ON CALCIUM ALUMINATE SOLUTIONS

From the experiments previously described in this paper, it would appear that metastable and supersaturated calcium aluminate solutions are formed in the early periods of the reaction of water with the high alumina cement and the 1:1, 3:5, and 5:3 calcium aluminates. Hydrated alumina and hydrated tricalcium aluminate subsequently precipitate from these solutions. The decomposition of the metastable monocalcium aluminate solutions was attended by an increase in pH in each case to about 11.75, even though the actual quantities of both lime and alumina in solution decreased as equilibrium was approached. The resulting solutions contained from 0.35 to 0.50 g of CaO and from 0.15 to 0.30 g of Al_2O_3 per liter. Although the total quantity of lime in solution decreased with the precipitation of hydrated tricalcium aluminate and hydrated alumina, yet the uncombined calcium hydroxide, or the lime in excess of that calculated to be in combination with the alumina in solution as monocalcium aluminate, increased. It was shown that the increase of this kind of lime resulted in the increase in pH to about 11.75. Therefore, as calcium hydroxide is a product of the hydrolysis of the calcium silicates occurring in Portland cement, it was decided to conduct a study of the subsequent changes in the aluminate solutions attended by further increasing concentrations of calcium hydroxide.

In order to study the effect of increasing concentrations of calcium hydroxide on an aluminate solution, a series of reaction mixtures containing, in each case, a liter of solution was prepared. The volume of the aluminate solution (containing 0.3075 and 0.3925 g Al_2O_3 and CaO per liter, respectively) was decreased in incre-

ments of 100 ml from one member of this series to another, with a proportionate increase in the volume of saturated calcium hydroxide (containing 1.176 g CaO per liter). The series of reaction mixtures was extended to that of a saturated calcium hydroxide solution, as this is the concentration of this base which is ultimately attained in the setting of Portland cement. The mixtures consisting of the calcium aluminate and calcium hydroxide solutions were set aside, for further observations, in tightly stoppered flasks in the air thermostat maintained at 30°. Since precipitation of very minute crystals started almost immediately upon the addition of the saturated calcium hydroxide solution to the aluminate solution, it was impossible to determine the pH of the mixture at this stage. After two weeks the resulting mixtures were filtered. Samples of the filtrate were taken for chemical determinations of lime and alumina and for pH determinations.

The data obtained in this investigation are recorded in Table 9. Column 1 gives the number of the reaction mixtures and columns 2 and 3 the proportioned volumes (in milliliters) of aluminate and calcium hydroxide solutions used in the preparation of the mixtures. Columns 4 and 5 give the grams per liter of alumina initially in solution and at equilibrium, respectively. The same data respecting lime in solution are tabulated in columns 6 and 7. The molar ratio, CaO/Al_2O_3, in the precipitate (column 12) was calculated from the data of columns 4, 5, 6, and 7. In Figure 14 the lime and alumina (expressed as grams per liter) at the start and at equilibrium are plotted against the volume composition of the solutions as given in columns 2 and 3. The pH values of the equilibrium solutions (column 11) are also plotted against this composition.

It is evident that increasing concentrations of calcium hydroxide result in the precipitation of increasing proportions of the total alumina and an increase in the pH. At a pH of 12.0, or above, the alumina is almost completely precipitated from solution. A portion of the lime is also precipitated with the alumina—presumably as a hydrated calcium aluminate. The molar ratio, CaO/Al_2O_3, in the precipitate, as computed from the composition of the solutions before and after precipitation, is recorded in column 12. The values are only approximate, since the computations involve a method of difference wherein the inherent errors may be fairly large. This is especially true of the values for the molar ratios of lime to alumina in the precipitate from mixtures Nos. 2 and 9, where the quantity of precipitate was very small. However, the molar ratio, $CaO/Al_2O_3 = 4.13$, of mixture No. 8 indicates that at the higher alkalinities a hydrated tetracalcium aluminate may be formed. But, in order to investigate the possible existence of such a compound, a new series of equilibrium mixtures was prepared from large volumes of aluminate and calcium

hydroxide solutions to obtain sufficient quantities of the precipitated material for more reliable chemical analyses.

Before discussing the results obtained, attention should be called to the remaining data of Table 9; that is, the relation between the pH of the equilibrium solutions as recorded in column 11 and the lime in the same solutions in excess of monocalcium aluminate, $CaO.Al_2O_3$, as given in column 9. The increase in pH is represented diagrammatically in Figure 13, which contains also the plotted values obtained heretofore for the less basic solutions obtained from the reaction of water on the calcium aluminates and high alumina cement. It is evident from Figure 13 that aluminic acid also behaves primarily as a monobasic acid at alkalinities higher than those heretofore studied in this investigation. This adds to the evidence in favor of the existence in aqueous solution of monocalcium aluminate, as brought out in the recent discussion of the constitution of aluminate solutions.

In the second series of reaction mixtures the aluminate solutions were obtained by filtering a mixture of high alumina cement and water which had stood a day. The clear filtrates were then mixed with the proportioned volume of clear calcium hydroxide solution, with the careful exclusion of the carbon dioxide of the air. As soon as the solutions were mixed, a "silken" precipitate appeared in each case, which settled after a day had elapsed. Four days later the bulk of the clear supernatent solution was siphoned from each mixture, with the careful exclusion of carbon dioxide of the air. Samples of the filtrates were taken for chemical analyses and for pH determinations. The mixture remaining was then filtered rapidly through a Büchner funnel. The precipitated material on the filter was pressed firmly between numerous sheets of filter paper and then washed with alcohol and ether. It was dried over anhydrous calcium chloride and analyzed for water (loss on ignition), alumina, and lime.

The analyses of the precipitate, together with the analyses and pH determinations of the resulting equilibrium solutions, are given in Table 10. It is seen that the molar ratio of lime to alumina in the precipitated material (column 13) increased with the pH of the equilibrium solution. At a $pH > 12.0$, this ratio is close to 4.0, indicating again that a tetracalcium aluminate may be formed. From the chemical analyses of the material, the composition apparently approaches that of a hydrated tetracalcium aluminate, $4CaO.Al_2O_3.12H_2O$. Le Chatelier [58] considered that a compound of this formula was formed in the setting of cement due to the reaction between anhydrous tricalcium aluminate, $3CaO.Al_2O_3$, and calcium hydroxide resulting from the hydrolysis of tricalcium silicate, as

$$3CaO.Al_2O_3 + Ca(OH)_2 + 11H_2O \rightarrow 4CaO.Al_2O_3.12H_2O$$

[58] Le Chatelier, Recherches Expérimentales sur la Constitution des Mortiers Hydrauliques, pp. 61 and 67, Thèse, Paris; 1887. English translation also prepared by J. L. Mack, New York; 1905.

the hydrated tetracalcium aluminate being the stable form in the presence of an excess of lime. More recently Lafuma [59] prepared a material of the same composition, $4CaO.Al_2O_3.12H_2O$, by the reaction of lime upon a calcium aluminate solution. He gave no optical properties of his material other than that under the microscope the crystals appeared as fine needles.

TABLE 9.—*Composition and pH of calcium aluminate—calcium hydroxide mixtures*

No.	Composition of mixture		Total alumina in solution g Al_2O_3 per 1		Total lime in solution g CaO per 1		Molar ratio, CaO/Al_2O_3, in solution at equilibrium	Lime in solution in excess CaO/Al_2O_3, g CaO per 1 at equilibrium	Observed E. M. F. at equilibrium at 30°	pH at equilibrium at 30°	Molar ratio, CaO/Al_2O_3, in precipitate at equilibrium
	Aluminate solution at start	Calcium hydroxide solution at start	A At start	B At equilibrium	A At start	B At equilibrium					
1	2	3	4	5	6	7	8	9	10	11	12
	ml	*ml*									
1	1,000	0	0.3075	0.3075	0.3925	0.3925	2.32	0.2234	0.9380	11.55	----------
2	900	100	.2768	.2500	.4708	.4425	3.22	.3050	.9455	11.67	3.06
3	800	200	.2460	.1875	.5492	.4770	4.62	.3749	.9510	11.77	2.22
4	700	300	.2153	.1440	.6275	.5370	6.78	.4578	.9550	11.83	2.31
5	600	400	.1845	.1000	.7059	.5850	10.6	.5300	.9590	11.90	2.95
6	500	500	.1537	.0370	.7912	.5895	29.0	.5691	.9621	11.95	3.14
7	400	600	.1230	.0075	.8626	.6770	106.0	.6739	.9664	12.02	2.92
8	300	700	.0922	.0025	.9410	.7370	----------	.7356	.9697	12.08	4.13
9	200	800	.0615	None.	1.0193	.9305	----------	.9305	.9743	12.15	2.48
10	0	1,000	----------	----------	1.1760	1.1760	----------	1.1760	.9830	12.30	----------

TABLE 10.—*Composition and pH of calcium aluminate—calcium hydroxide mixtures and chemical analyses of the resulting precipitates*

No.	Composition of mixture		Total alumina in solution, g Al_2O_3 per 1 at equilibrium	Total lime in solution, gCaO per 1 at equilibrium	Lime in solution in excess CaO/Al_2O_3, gCaO per 1 at equilibrium	Observed E. M. F. at equilibrium at 30°	pH at equilibrium at 30°	Analysis of precipitate (percentage composition)				Molar ratio, CaO/Al_2O_3 in precipitate
	Aluminate solution at start	Calcium hydroxide solution at start						Al_2O_3	CaO	H_2O	Total	
	Liters	*Liters*										
1	10	2	0.3860	0.4600	0.2477	0.9440	11.65	26.56	35.69	37.36	99.61	2.44
2	8	4	.1300	.5875	.5160	.9585	11.89	24.42	37.65	36.77	98.84	2.80
3	6	6	.0770	.6600	.6168	.9625	11.96	19.02	40.49	39.60	99.11	3.87
4	4	8	.0250	.7470	.7332	.9675	12.04	18.71	40.50	39.85	99.06	3.93
5	2	10	.0000	.9940	.9940	.9755	12.17	18.78	41.40	39.63	99.81	4.01
Theoretical composition 4 CaO. Al_2O_3. 12 H_2O								18.82	41.34	39.84	100.00	4.00

A microscopic examination of several of the precipitates which had a molar ratio of lime to alumina close to 4 was undertaken in the present investigation. The material was found to be composed almost wholly of very minute crystals, apparently plates which often appeared as fibers or fine needles when turned on edge. These

[59] Lafuma, Recherches sur les aluminates de calcium et sur leurs combinaisons avec le chlorure et le sulfate de calcium. Thèse, Paris, p. 22, 1925. Also copies in Le Ciment, p. 174, May, 1925.

fibers showed positive elongation. It was very difficult to obtain exact indices, due to the fineness of grain of the crystals. The omega (or gamma) index was about 1.532 ± 0.005 and the epsilon (or alpha) index about 1.505 ± 0.005. These values are approximately the same as those obtained for hydrated tricalcium aluminate, already described. No amorphous substances could be found, but the fineness of grain of the crystalline material and its tendency to form aggregates may have obscured small amounts of such materials. The samples examined showed no reaction with White's solution (used for the detection of "free" lime) after one hour of contact

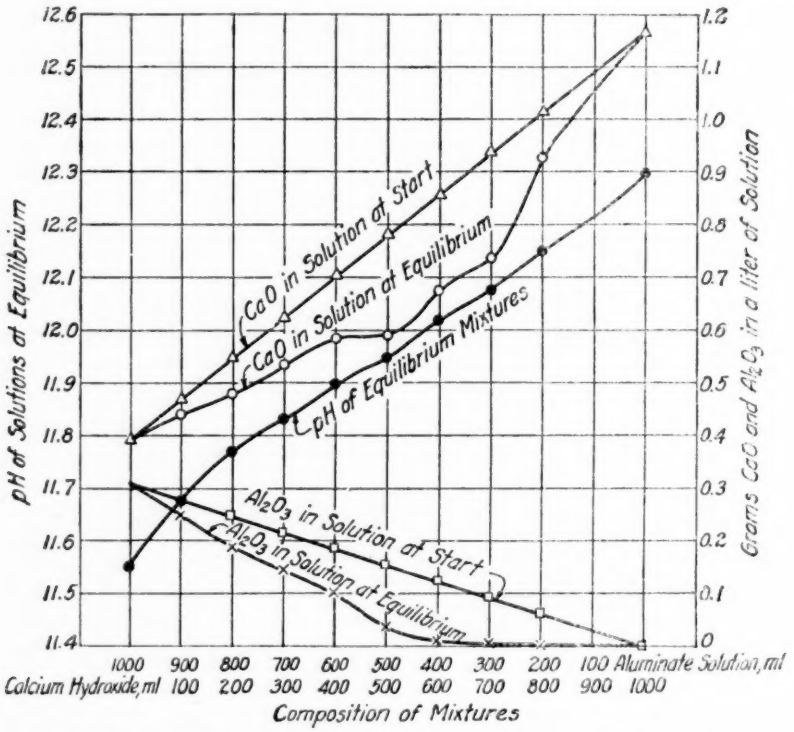
pH of Solutions at Equilibrium
Grams CaO and Al_2O_3 in a liter of Solution
CaO in Solution at Start
CaO in Solution at Equilibrium
pH of Equilibrium Mixtures
Al_2O_3 in Solution at Start
Al_2O_3 in Solution at Equilibrium
Calcium Hydroxide, ml
Aluminate Solution, ml
Composition of Mixtures

FIG. 14.—*Showing the changes in the composition and pH of an aluminate solution attended by increasing concentrations of calcium hydroxide*

with this reagent. The microscopic examination and the interpretation of such in the case of very fine grained material is very difficult. It would be of interest to establish more conclusively the identity of this and other hydrated calcium aluminates in future investigations. The use of X-ray patterns and other methods of attack may eventually throw more light upon this subject. The present study, however, indicates that a hydrated tetracalcium aluminate, $4CaO.Al_2O_3.12H_2O$, may be formed by the reaction of an excess of calcium hydroxide on a calcium aluminate solution if the pH of the resulting equilibrium solution becomes greater than 12.0.

2. REACTION OF CALCIUM SILICATES ON ALUMINATE SOLUTIONS

(A) REACTION OF TRICALCIUM SILICATE, $3CaO.SiO_2$, ON ALUMINATE SOLUTIONS

From the study of the reaction of calcium hydroxide on an aluminate solution it was shown that increasing concentrations of calcium hydroxide result in the precipitation of increasing proportions of the total alumina, and that at a pH greater than 12.0 the alumina is practically all precipitated from solution as a hydrated calcium aluminate approaching, in composition, $4CaO.Al_2O_3.12H_2O$. Since calcium hydroxide is a product of the hydrolysis of tricalcium silicate, which occurs in Portland cement, it was decided to make up a series of mixtures of anhydrous tricalcium silicate and aluminate solutions to see if the resultant changes were actually analogous to those observed in the study of the reaction of increasing concentrations of calcium hydroxide on aluminate solutions. The procedure was to note the changes in the pH and chemical composition of an aluminate solution to which some anhydrous tricalcium silicate had been added. Accordingly, a series of reaction mixtures were prepared which contained 500 ml of an aluminate solution and 1 g anhydrous $3CaO.SiO_2$, ground to a degree of fineness such that about 90 per cent passed a No. 200 sieve. The aluminate solution was prepared by shaking some high alumina cement with water, in the manner already described. This solution had a pH of 11.50 and contained 0.3110 g Al_2O_3 and 0.3740 g CaO per liter. The reaction mixtures were kept in well-stoppered flasks which were placed in the air thermostat maintained at 30°. In order to get further information and to see whether or not the reactions occurring in the mixtures of the silicate with aluminate solutions may be in any way analogous to those proceeding in mixtures of this silicate with water, a second series of mixtures was likewise prepared, which consisted of 1 g $3CaO.SiO_2$ in 500 ml of distilled water. This new series also was placed in the air thermostat. The mixtures were shaken from time to time, and on successive days aliquots of the filtrates from separate reaction mixtures of both series were taken for analyses, and the dissolved alumina, lime, and the pH were determined.

It was observed that the particles of tricalcium silicate started to swell within 30 minutes after being placed in water. At the end of the first day they had swollen considerably. The swelling then continued more slowly, and at the same time increasing quantities of lime (calcium hydroxide) were dissolved as a result of the continued hydrolysis of this silicate. Accordingly, the pH of the solution increased. This is shown in the data of Table 11 and graphically represented in Figure 13, previously described.

However, the tricalcium silicate behaved differently in the aluminate solution than in water. In the aluminate solution there was no apparent swelling at the end of the first day. The material adhered

slightly to the bottom of the flask, such adherence increasing with time. After three days small spherulites of crystals—presumably a hydrated calcium aluminate—appeared on the bottom of the flask and after five days were visible on the walls of the container. The changes in the composition of the solutions are recorded in Table 12 and represented graphically in Figure 15. It can be seen that the pH increased slowly as time progressed, while the alumina in solution decreased, at first rapidly, and then more slowly, until it reached a value of about 0.02 g per liter. The latter value remained unchanged during the next 11 days.

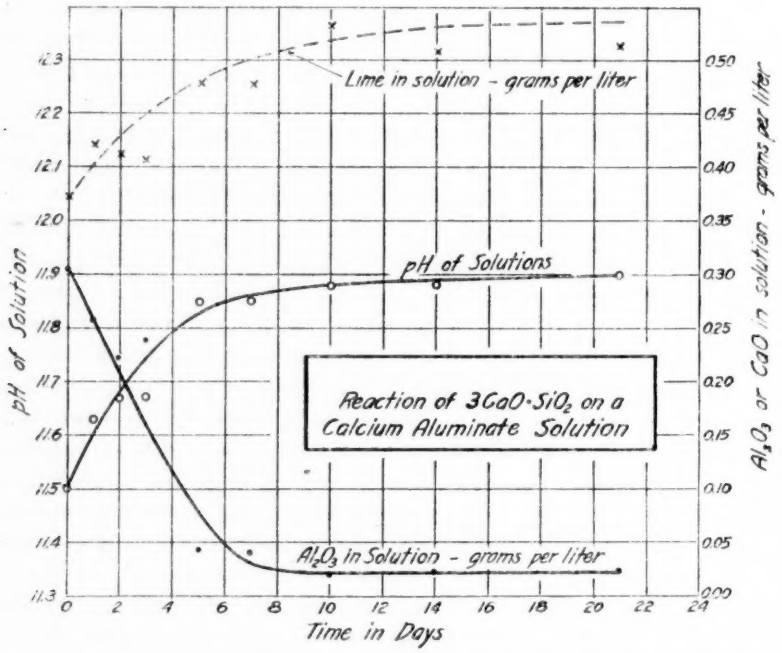

FIG. 15.—*Showing the change in the composition and pH of an aluminate solution resulting from the hydrolysis of tricalcium silicate*

TABLE 11.—*Hydrolysis of tricalcium silicate in water at 30°*

[1 g $3CaO.SiO_2$ per 500 ml water]

	Time	Lime in solution, g CaO per l	Observed E. M. F. at 30°	pH of solution at 30°
	Days			
No. 2	1	0.3829	0.9525	11.79
No. 3	2	.4150	.9547	11.83
No. 4	3	.4498	.9562	11.85
No. 5	5	.4734	.9579	11.88
No. 6	7	.5000	.9590	11.90
No. 7	10	.5110	.9590	11.90
No. 8	14	.5236	.9598	11.91
No. 9	21	.5500	.9615	11.94
No. 10	28	.5821	.9633	11.97

TABLE 12.—*Hydrolysis of tricalcium silicate in aluminate solution at 30°*

[1 g $3CaO.SiO_2$ per 500 ml aluminate solution]

	Time	Alumina in solution, g Al_2O_3 per l	Lime in solution, g CaO per l	Lime in solution in excess $CaO.Al_2O_3$, g CaO per l	Observed E. M. F. at 30°	pH of solution at 30°
	Days					
No. 1	0	0.3110	0.3740	0.2030	0.9354	11.50
No. 2	1	.2575	.4235	.2819	.9430	11.63
No. 3	2	.2220	.4175	.2954	.9450	11.67
No. 4	3	.2400	.4100	.2780	.9451	11.67
No. 5	5	.0425	.4800	.4566	.9559	11.85
No. 6	7	.0410	.4790	.4564	.9560	11.85
No. 7	10	.0190	.5325	.5220	.9580	11.88
No. 8	14	.0240	.5063	.4935	.9578	11.88
No. 9	21	.0240	.5135	.5003	.9588	11.90

From the above data it is evident that the changes in the composition of the aluminate solutions in the presence of tricalcium silicate were analogous to those attended by increasing concentrations of calcium hydroxide, as previously recorded in Tables 9 and 10. Thus, by using a small quantity of tricalcium silicate, it was possible to follow the changes in the aluminate solutions, and such changes may be analogous to those occurring in the setting of Portland cement and which take place within a few minutes due to the relatively higher concentrations of calcium silicates. It has previously been observed that small amounts of alumina may be found in the solutions obtained by shaking Portland cement with water for a few minutes. At later periods the degree of alkalinity ($pH > 12.0$) of such solutions reaches a value sufficiently high to precipitate the alumina completely from solution.

(b) REACTION OF BETA DICALCIUM SILICATE, β $2CaO.SiO_2$ ON ALUMINATE SOLUTIONS

Klein and Phillips,[60] in their studies of the hydration of Portland cement, made up a series of mixtures of about three parts of beta dicalcium silicate (beta-orthosilicate) to one each of the following: Tricalcium aluminate, 5:3 calcium aluminate, and monocalcium aluminate. They noted that when these mixtures were placed on microscopic slides the aluminates started to hydrate soon after the addition of water to the material, with the formation of needles and plates of hydrated tricalcium aluminate in all mixes. They also observed some amorphous hydrated alumina in the mixtures of the beta dicalcium silicate with the 5:3 and 1:1 calcium aluminate. The silicate started to hydrate within two days with the formation of amorphous gelatinous material, which later covered the whole slide.

It will be recalled that the formation of hydrated tricalcium aluminate and hydrated alumina in the setting of the 5:3 and 1:1 calcium aluminates is in agreement with the conclusion of the present investigation, which also gives the additional information that the

[60] B. S. Tech. Paper No. 43, p. 42.

hydrated alumina and hydrated tricalcium aluminate result from the decomposition of metastable monocalcium aluminate solutions formed in the early periods of the reaction.

Klein and Phillips also state, "No reason for the behavior of the aluminates in hastening the hydration of beta-orthosilicate has been found, other than it is simply a case of the silicate being more soluble in the aluminate solution than in water, and that a saturated solution is formed with subsequent precipitation of the amorphous hydrated silicate."

It seemed that further light might be thrown upon this question by following the changes in the pH and chemical composition of an aluminate solution to which some beta-calcium orthosilicate had been added, and comparing these changes to those which take place in mixtures of water and the same silicate. The method of procedure was essentially the same as that already described in the investigation of the reaction of the tricalcium silicate.

The anhydrous $\beta 2CaO.SiO_2$ was ground to a degree of fineness such that about 90 per cent passed a No. 200 sieve. The aluminate solution had a pH of 11.48 and contained 0.3125 g Al_2O_3 and 0.3580 g CaO per liter. In this manner the following series of reaction mixtures were then prepared and kept in well-stoppered flasks which were placed in the air thermostat, maintained at 30°.

Series A. 1 g $\beta 2CaO.SiO_2$ to 500 ml water.
Series B. 2 g $\beta 2CaO.SiO_2$ to 500 ml water.
Series C. 5 g $\beta 2CaO.SiO_2$ to 500 ml water.
Series D. 1 g $\beta 2CaO.SiO_2$ to 500 ml aluminate solution.
Series E. 2 g $\beta 2CaO.SiO_2$ to 500 ml aluminate solution.
Series F. 5 g $\beta 2CaO.SiO_2$ to 500 ml aluminate solution.

The above mixtures were shaken occasionally, and at different time intervals aliquot portions of the filtrates from separate reaction mixtures were taken for analyses and pH determinations.

It may be recalled that the tricalcium silicate started to swell within 30 minutes after being placed in water. No swelling of the dicalcium silicate, however, was noted until after 28 days, when this material then adhered to the bottom of the flask and appeared slightly swollen. Simultaneously, the lime liberated to the solution increased with a consequent increase in pH. This is shown in the data of Table 13 and graphically represented in Figure 13, previously described. The mixtures containing the higher percentage of dicalcium silicate gave the higher pH values.

In the aluminate solutions the dicalcium silicate was apparently still more inert. This silicate under these conditions did not swell even at the later periods, and the material has shown no tendency to adhere or "set" even after an elapse of two years. Furthermore, the composition and the pH of the aluminate solution, in which the

silicate was placed, remained practically unchanged, as can be observed from the data of Table 13. This indicates that the dicalcium silicate has hydrolyzed but little in such solutions, since it has been shown previously that calcium hydroxide (a product of the hydrolysis of the silicates in water) reacts with an aluminate solution with the continuous precipitation of alumina (as a hydrated aluminate) and an increase in the pH as the quantity of calcium hydroxide is increased. The repression of the hydrolysis of the dicalcium silicate by the aluminate solution is shown even more clearly by a comparison of Tables 13 and 14. Even after one takes into consideration the lime which might have been removed from the aluminate solution in the precipitation of hydrated tricalcium aluminate, there is still a marked difference in the lime dissolved by the water over that liberated to the aluminate solution. For example, in Table 14 it is seen that the alumina precipitated from solution 11, of the D series, after 60 days was 0.3125 − 0.2860, or 0.0265 g per liter. This should remove 0.0437 g of CaO if $3CaO.Al_2O_3$ (H_2O) were precipitated. The actual decrease of CaO was but 0.3580 − 0.3445, or 0.0135 g per liter. This means that 0.0437 − 0.0135, or 0.0302 g was supplied by the hydrolysis of the $2CaO.SiO_2$. When compared to the lime given up to the water (see Table 13, A series, No. 11), after the same lapse of time, of 0.1950 g per liter, it can be seen that there is a difference of 0.1950 − 0.0302 or 0.1648 g. This difference is even greater in those mixtures containing a higher percentage of dicalcium silicate.

It is realized that the above results throw but little light on the problem regarding the rôle played by the dicalcium silicate in the processes of setting and hardening of Portland cement. Undoubtedly, both hydrolysis and hydration of dicalcium silicate are concerned in such processes, but which of these is of the more importance is not known. The above experiments would indicate that the dicalcium silicate does not hydrolyze (that is, liberate calcium hydroxide) as readily in a calcium aluminate solution as in water and that the separate particles of the silicate have but little tendency to adhere and "set" in an aluminate solution.

On the other hand, Klein and Phillips concluded from microscopical observations that the dicalcium silicate hydrates more readily in mixtures containing the various anhydrous aluminates than in water. Evidently, then, the presence of an excess of the aluminates is a factor of moment. Bates [61] found that tricalcium aluminate, when used to replace about 19 per cent of the dicalcium silicate (which is approximately the amount of aluminate present in Portland cement), adds somewhat to the strength of the latter at later periods. Apparently the whole problem is complicated, and the answer of the apparent hastening of the hydration of the dicalcium silicate may be found to

[61] B. S. Tech. Paper No. 78; see Tables 2 and 5.

be more than simply a case of the silicate being relatively more soluble in the aluminate solution than in water.

It would be of interest to study further the setting and hardening of beta dicalcium silicate in the presence of each of the calcium aluminates as well as in aluminate solutions of different composition than the one used in the above investigation.

TABLE 13.—*Hydrolysis of beta dicalcium silicate in water at 30°*

	Time	Lime in solution g CaO per l	Observed E. M. F. at 30°	pH of solution at 30°
A SERIES. 1 g $2CaO \cdot SiO_2$ PER 500 ml WATER				
	Days			
No. 2	1	0.1114	0.9048	11.00
No. 3	2	.1162	.9127	11.13
No. 4	3	.1169	.9138	11.15
No. 5	5	.1184	.9149	11.16
No. 6	7	.1169	.9153	11.17
No. 7	10	.1162	.9152	11.17
No. 8	14	.1177	.9145	11.16
No. 9	21	.1169	.9142	11.15
No. 10	28	.1177	.9152	11.17
No. 11	60	.1950	.9354	11.51
B SERIES. 2 g $2CaO \cdot SiO_2$ PER 500 ml WATER				
No. 3	2	0.1232	0.9160	11.18
No. 10	28	.2367	.9450	11.66
C SERIES. 5 g $2CaO \cdot SiO_2$ PER 500 ml WATER				
No. 3	2	0.1560	0.9250	11.33
No. 10	28	.4664	.9570	11.87

TABLE 14.—*Hydrolysis of beta dicalcium silicate in aluminate solution at 30°*

	Time	Alumina in solution g Al_2O_3 per l	Lime in solution g CaO per l	Lime in solution in excess $CaO \cdot Al_2O_3$, g CaO per l	Observed E. M. F. at 30°	pH of solution at 30°
D SERIES. 1 g $2CaO \cdot SiO_2$ PER 500 ml ALUMINATE SOLUTION						
	Days					
No. 1	0	0.3125	0.3580	0.1761	0.9338	11.48
No. 2	1	.3050	.3555	.1877	.9355	11.51
No. 3	2	.3040	.3480	.1808	.9352	11.51
No. 4	3	.2950	.3430	.1807	.9344	11.49
No. 5	5	.3010	.3500	.1844	.9363	11.52
No. 6	7	.2995	.3520	.1873	.9363	11.52
No. 7	10	.2970	.3480	.1846	.9354	11.51
No. 8	14	.2875	.3520	.1937	.9362	11.52
No. 9	21	.2900	.3450	.1855	.9355	11.51
No. 10	28	.2895	.3480	.1888	.9359	11.52
No. 11	60	.2860	.3445	.1882	.9350	11.50
E SERIES. 2 g $2CaO \cdot SiO_2$ PER 500 ml ALUMINATE SOLUTION						
No. 3	2	0.2930	0.3405	0.1793	0.9348	11.50
No. 10	28	.2700	.3460	.1975	.9356	11.51
F SERIES. 5 g $2CaO \cdot SiO_2$ PER 500 ml ALUMINATE SOLUTION						
No. 3	2	0.2755	0.3450	0.1935	0.9350	11.50
No. 10	28	.2780	.3450	.1921	.9364	11.52

IV. CALCIUM CHLOR-ALUMINATES

1. ELECTROMETRIC TITRATION STUDY OF ALUMINUM CHLORIDE WITH CALCIUM HYDROXIDE AND AN INVESTIGATION OF CALCIUM CHLOR-ALUMINATES

In the discussion of the constitution of aluminate solutions it was shown how previous investigators, by the construction of titration curves from electromotive-force measurements, had brought out the salient characteristics of monobasic aluminic acid. The earlier studies were, for the most part, electrometric titrations of aluminum salts with alkalies. It seemed desirable, therefore, to make a complete electrometric titration of an aluminum salt with calcium hydroxide, with the belief that additional information would be obtained relative to the constitution of the calcium aluminates in aqueous solutions. Chronologically, this study was completed before the investigation of the reaction of water on the calcium aluminates, herein previously described, was started. In fact, the electrometric titration study laid the foundation for many of the methods of procedure which were later to be applied to the more general problem. In the meantime, Britton [62] published the results of his electrometric titrations of aluminum salts with alkaline earth hydroxides, including a titration of aluminum sulphate with calcium hydroxide. It is gratifying to find a general agreement in the results of his investigation with those of this laboratory. However, since the present study deals more extensively with the reactions at the higher alkalinites (that is, pH > 10.0) and involves a consideration of the formation of the calcium chlor-aluminates in an electrometric titration study of aluminum chloride with calcium hydroxide, additional knowledge of the reaction of the aluminates has been obtained. Furthermore, the investigation herein described also presents the changes in the composition of the solutions resulting from the precipitation of the solid phases during the titration, together with the chemical composition and optical properties of the hydrated calcium chlor-aluminate.

Several preliminary titrations were made from continuous electrode measurements carried out in a bottle into which were led the hydrogen electrodes as previously described, the gas inlet and outlet, a goose-neck siphon from the saturated calomel half cell, a motor-driven glass stirrer, and a burette tip. The other parts of the potentiometric system have already been described. However, in the more alkaline regions it was found that the potentials, obtained after each addition of calcium hydroxide, were not constant. The drift was of uncertain nature and was undoubtedly due to properties of the solid phases precipitating from solution and the general complexity of the proc-

[62] J. Chem. Soc. (London), p. 422; 1927.

esses occurring. Similar drifts of potential have been noted by Theriault and Clark [63] in their electrometric titrations concerning the studies of the relation of the hydrogen-ion concentrations to the formation of floc in alum solutions.

Consequently, a series of mixtures consisting of varying amount of aluminum chloride and calcium hydroxide were prepared and set aside in well-stoppered flasks, and, after equilibrium had been reached on standing, an electrometric titration curve was obtained by measuring the potentials of aliquot portions of each mixture separately transferred to the electrode vessel, following the procedure formerly described. The alumina remaining in solution after equilibrium had been attained was also determined from separate aliquots.

All materials were first purified with the greatest of care, and the solutions of $AlCl_3$ and $Ca(OH)_2$ used in the preparation of the above mixtures were both 0.043 *N*.

TABLE 15.—*Electrometric titration of $AlCl_3$ with $Ca(OH)_2$*

No.	Composition of equilibrium mixture		Mols CaO per mol Al_2O_3 in mixture	Total alumina at start, g Al_2O_3 per l	Alumina in solution at equilibrium, g Al_2O_3 per l	Observed E. M. F. at equilibrium at 30°	pH at equilibrium at 30°	Remarks
	$AlCl_3$ (0.043 *N*) at start	$Ca(OH)_2$ (0.043 *N*) at start						
	ml	*ml*						
1	1,000	0	0.00	0.7300	0.7300	0.4667	3.71	Solution clear.
2	900	100	.33	.6570	.6570	.4726	3.81	Do.
3	800	200	.75	.5840	.5840	.4763	3.87	Do.
4	700	300	1.29	.5110	.5110	.4825	3.97	Do.
5	600	400	2.00	.4380	.4380	.4766	3.87	Do.
6	550	450	2.45	.4015	.4015	.4810	3.95	Do.
7	530	470	2.66	.3869	.3860	.4816	3.96	Faint opalescence.
8	520	480	2.77	.3796	.3510	.4951	4.16	Distinct opalescence.
9	510	490	2.88	.3723	None.	.5935	5.82	Floc of $Al(OH)_3$.
10	500	500	3.00	.3650	None.	.7290	8.07	Do.
	500	500	3.00	.3650	None.	.7158	7.85	Do.
	500	500	3.00	.3650	None.	.7388	8.23	Do.
11	475	525	3.32	.3453	.0750	.8870	10.70	Do.
12	450	550	3.67	.3285	.0850	.8958	10.85	Do.
13	440	560	3.82	.3219	.0950	.9061	11.02	Decreasing amount of floc.
14	430	570	3.98	.3139	.1560	.9000	10.92	Do.
15	420	580	4.13	.3066	.3066	.9015	10.94	Floc disappeared, solution clear.
16	410	590	4.31	.2993	.2993	.9103	11.09	Solution clear.
17	400	600	4.50	.2930	.2930	.9163	11.19	Do.
18	380	620	4.90	.2774	.2774	.9258	11.34	Do.
19	360	640	5.33	.2628	.2480	.9290	11.40	First precipitation of chlor-aluminate.
20	350	650	5.57	.2555	.1880	.9320	11.45	Precipitate of chlor-aluminate.
21	300	700	7.00	.2190	.1110	.9402	11.59	Do.
22	250	750	9.00	.1825	.0525	.9477	11.71	Do.
23	200	800	12.00	.1460	.0200	.9582	11.88	Do.
24	150	850	17.00	.1095	.0060	.9615	11.94	Do.
25	100	900	27.00	.0750	Trace.	.9682	12.05	Do.
26	50	950	57.00	.0365	None.	.9724	12.12	Do.
27	0	1,000	----------	----------	----------	.9818	12.29	Solution clear.

[63] U. S. Pub. Health Rep., 38, p. 181; 1923.

The data obtained in this investigation are recorded in Table 15. Column 1 gives the number of the reaction mixture and column 2 and 3 the proportioned volumes (in milliliters) of the 0.043 *N.* $AlCl_3$ and 0.043 *N.* $Ca(OH)_2$ used in their preparation. Column 4 gives the mols CaO per mol Al_2O_3, figured from the volume and normality relations of the $AlCl_3$ and $Ca(OH)_2$. Columns 5 and 6 contain the grams per liter of alumina initially in solution and at equilibrium, respectively. The observed e. m. f. and computed pH of the equilibrium solutions are recorded in columns 7 and 8. In Figure 16 the alumina (expressed as grams per liter) at the start and at equilibrium is plotted against the volume composition of the solution as given in

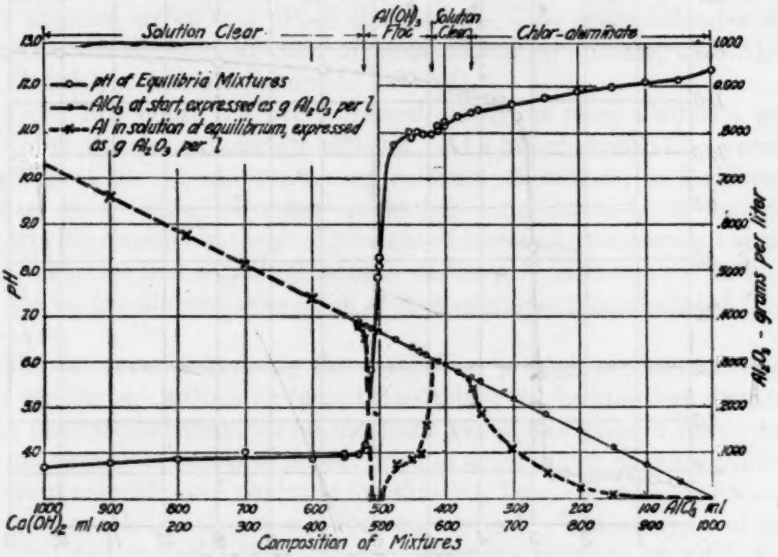

FIG. 16.—*Electrometric titration curve of aluminum chloride with calcium hydroxide, showing the regions in which the different phases are separately precipitated*

columns 2 and 3 of Table 15. The pH values of the equilibrium solutions are also plotted against this composition. In Figure 17 the pH values are plotted against the mols CaO per mol Al_2O_3 as recorded in column 4 of the same table.

If these curves are compared with those published by previous investigators,[64] there will be found a general agreement in the main features, particularly in the regions less alkaline than pH 10.0. However, it appears advisable to discuss briefly some of the salient factors pertaining to the reactions at the lower alkalinities for a more complete understanding of the subsequent changes occurring in the

[64] Hildebrand, J. Am. Chem. Soc., **35**, p. 864; 1913; Blum, ibid., **35**, p. 1499; 1913; Theriault and Clark, U. S. Pub. Health Rep., **38**, p. 181; 1923; Britton, J. Chem. Soc. (London), p. 422; 1927.

solutions more alkaline than pH 10.0. Thus, an aqueous solution of $AlCl_3$ is distinctly acid, as shown by a pH of 3.71 for the 0.043 *N* solution. As 0.043 *N* $Ca(OH)_2$ of pH 11.29 was added to this solution, the pH of the resulting mixture at first increased but slightly and the solutions remained clear; only opalescence was produced, even after the addition of 2.66 equivalents of $Ca(OH)_2$ per atom of aluminum had been added. This is represented in Table 15 by mixture No. 7, which contained 530 ml $AlCl_3$ and 470 ml $Ca(OH)_2$. The opalescence increased when more $Ca(OH)_2$ was added, until a floc of Al

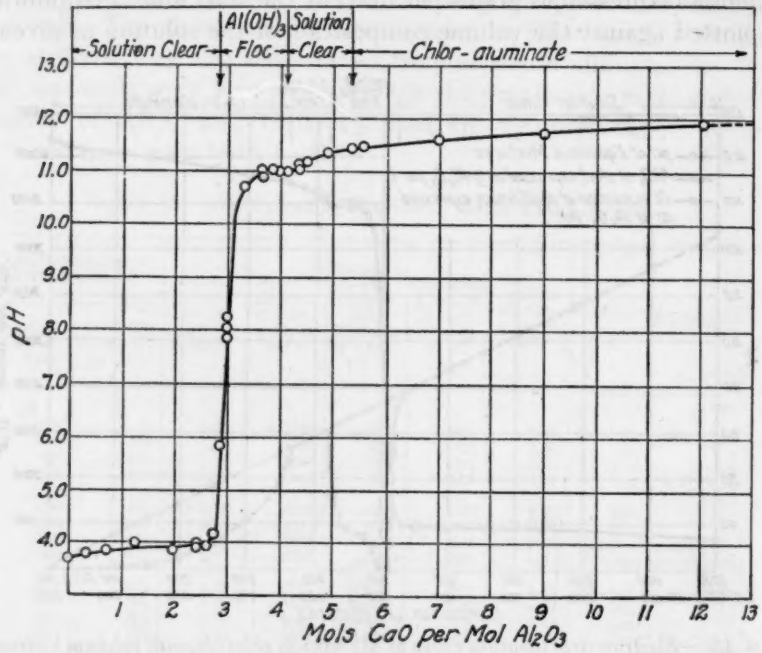

FIG. 17.—*Electrometric titration curve of aluminum chloride with calcium hydroxide, showing the pH values as a function of the mols CaO added per mol* Al_2O_3

$(OH)_3$ gradually appeared at a pH of 5.82 when 2.88 equivalents of $Ca(OH)_2$ had been added. When three mols $Ca(OH)_2$ had been added to two of $AlCl_3$ (mixture No. 10 of 500 ml $Ca(OH)_2$:500 ml $AlCl_3$) the pH had increased to 8.0. This represents just enough $Ca(OH)_2$ to complete the reaction

$$2AlCl_3 + 3Ca(OH)_2 \rightleftharpoons 2Al(OH)_3 + 3CaCl_2$$

The rate of floc formation was greater at pH 8.0 than at pH 5.82. This was also noted by Miller,[65] who showed, furthermore, that coagulation was dependent not only upon the concentration of the hydro-

[65] U. S. Pub. Health Rep., 40, p. 351; 1925.

genions, but also upon the anions present. Thus, the sulphate ion has a stronger coagulating effect than the chloride ion. In general, however, the "precipitation" in the sense of the chemical formation of $Al(OH)_3$ (which at first may not actually coagulate) begins at pH 4.0 and is complete before pH 8.0. Appreciable resolution of the floc of $Al(OH)_3$ occurs soon after pH 8.0 is passed. Blum has shown that an appreciable amount of alumina was always found dissolved in any solution in which the pH is greater than 9.0 but was a minimum between pH 6.5 and 7.5, points approximately defined by the color change of methyl red and of rosolic acid. The $Al(OH)_3$ redissolved completely when approximately another equivalent of $Ca(OH)_2$ had been added, the redissolving being indicated by a slight inflection of the titration curve at a pH of about 10.9. This again indicates the existence in aqueous solution of monocalcium aluminate, $CaO.Al_2O_3$ or $Ca(AlO_2)_2$, and the aluminate ion, AlO_2^-.

From this point the pH increased slowly as more $Ca(OH)_2$ was added to the clear aluminate solution. At a pH of about 11.4 a purely crystalline precipitate containing calcium, aluminum, and chlorine began to separate. Further increasing concentrations of calcium hydroxide resulted in the precipitation of increasing proportions of the total alumina and a gradual increase in the pH, until at a pH of 12.0, or above, the alumina was again almost completely percipitated from solution.

The mixtures containing the crystalline precipitates were filtered rapidly through a Büchner funnel in a cabinet free from carbon dioxide. The precipitated material on the filter paper was pressed firmly between numerous sheets of paper, dried in a desiccator over anhydrous calcium chloride, and analyzed for alumina, lime, chlorine, and water (loss on gentle ignition over a Bunsen burner). The analyses of the precipitated material from the proportionate volumes of $AlCl_3$ and $Ca(OH)_2$, represented by mixtures Nos. 20, 21, and 22 of Table 15, are recorded in Table 16, together with the total calcium chloride (expressed in terms of normality) in solution directly upon mixing. The composition of the precipitate was calculated from the analyses on the assumptions that a computed portion of calcium was combined with all of the chlorine as $CaCl_2$, and the remainder was present as CaO in a hydrated calcium chlor-aluminate. Evidently these assumptions were valid, since the compositions then totaled very close to 100 per cent.

TABLE 16.—*Analysis of precipitates from $AlCl_3$:$Ca(OH)_2$ mixtures*

	No. (see Table 15)		
	21	22	23
Composition of mixture:			
$AlCl_3$ 0.043 *N*.....ml	600	500	400
$Ca(OH)_2$ 0.043 *N*.....do	1,400	1,500	1,600
Normality $CaCl_2$ in mixture	.0129	.0107	.0086
pH of mixture	11.59	11.71	11.88
Composition of precipitate:			
Al_2O_3	18.76	18.70	18.89
CaO	31.01	32.56	33.17
$CaCl_2$	15.98	14.78	13.32
H_2O	[1] 34.25	34.12	34.66
Total	100.00	100.16	100.04
Molar ratio $CaCl_2/Al_2O_3$	.78	.73	.66
Molar ratio CaO/Al_2O_3	3.00	3.16	3.19
Molar ratio H_2O/Al_2O_3	10.32	10.32	10.37

[1] H_2O by difference.

Kühl and Ulbrich [66] have shown that when solutions of aluminum chloride and calcium hydroxide interact precipitates containing chlorine may be formed in which the $CaCl_2$ content varies appreciably from $^1/_2$ to 1 mol for each mol of Al_2O_3. However, since the precipitates contain in addition about three mols CaO for each mol Al_2O_3, they have suggested as the limits for the composition of the precipitates, $3CaO.Al_2O_3.^1/_2CaCl_2$ and $3CaO.Al_2O_3.1CaCl_2$. It should be noted that the composition of the precipitates as given in Table 16 fall within these limits. However, the molar ratio $CaCl_2/Al_2O_3$, in these precipitates decreased with a simultaneous decrease in the total concentration of chloride ($CaCl_2$) in the mixture. This suggests the idea that the chlor-aluminate, $3CaO.Al_2O_3.CaCl_2(H_2O)$, may be partially decomposed into $CaCl_2$ and $3CaO.Al_2O_3(H_2O)$ (hydrated tricalcium aluminate) according to the following equation:

$$3CaO.Al_2O_3.CaCl_2(H_2O) \rightleftarrows 3CaO.Al_2O_3(H_2O) + CaCl_2,$$

in which case the products of the reaction would be a mixture of the chlor-aluminate and aluminate with a chemical composition falling within the above limits, depending upon the extent of decomposition. If this explanation is correct, then increasing concentrations of $CaCl_2$ should force the reaction from right to left, and there should be some definite concentration of $CaCl_2$ above which $3CaO.Al_2O_3.CaCl_2(H_2O)$ would be a stable phase. This was found to be the case, as will be shown in the following study of the formation and composition of calcium chlor-aluminates resulting from the reaction of calcium chloride or calcium aluminate solutions.

[66] Zement, **14**, pp. 859-861, 880-882, 898-901, 917; 1925.

2. CALCIUM CHLOR-ALUMINATE FROM THE REACTION OF CALCIUM CHLORIDE ON ALUMINATE SOLUTIONS

It has been shown that calcium aluminate solutions are formed from the reaction of water upon the anhydrous calcium aluminates or high alumina cement, and that the alumina in these solutions is apparently combined with a portion of the lime as monocalcium aluminate with the remainder of the lime existing in solution as calcium hydroxide. Also, in the electrometric titration study of $AlCl_3$ and $Ca(OH)_2$, it was shown that under certain conditions sparingly soluble calcium chlor-aluminates are precipitated. Therefore, it was concluded that such chlor-aluminates might also be obtained by the addition of calcium chloride to an aluminate solution, provided there was also sufficient calcium hydroxide in solution to supply the necessary three mols CaO required in the precipitation of $3CaO.Al_2O_3.XCaCl_2(H_2O)$. Furthermore, it can be seen that the pH of the solutions must decrease if the chlor-aluminates are precipitated in this manner with the removal of a portion of the calcium hydroxide from solution. Finally, a study of the subsequent changes attended by increasing concentrations of calcium chloride should supply the additional information as to the concentration of calcium chloride necessary for the sole formation of $3CaO.Al_2O_3.CaCl_2(H_2O)$, as previously discussed in relation to the equation

$$3CaO.Al_2O_3.CaCl_2(H_2O) \rightleftarrows 3CaO.Al_2O_3.(H_2O) + CaCl_2$$

Consequently, an aluminate solution was prepared and analyzed according to the procedure previously described. This solution contained 0.3005 g Al_2O_3 and 0.3985 g CaO per liter, respectively, which gave a pH of 11.52. A crystalline precipitate was formed immediately upon the addition of weighed quantities of C. P. calcium chloride to separate portions of this aluminate solution in each case. After several days the resultant mixtures, which had been kept in well-stoppered flasks, were filtered with the aid of suction. The precipitated material was dried and analyzed by methods heretofore described, and the pH of the filtrate was determined.

From columns 1 and 2 of Table 17 it is seen that the pH of the aluminate solutions decreased with increasing concentrations of calcium chloride, until about 3 per cent of this salt had been added, after which it remained constant with further increasing concentrations of calcium chloride. This is shown graphically in Figure 18. Undoubtedly this decrease in pH is due to the continuous removal of a portion of the calcium hydroxide from solution as increasing quantities of the calcium chlor-aluminate are precipitated.

Table 18 shows that the per cent $CaCl_2$ in the precipitate is a direct function of the total amount of $CaCl_2$ in the mixture. When the normality of the $CaCl_2$ in the mixture is greater than 0.5 (equiva-

lent to about 3 per cent $CaCl_2$ by weight) the composition of the precipitated material agrees very closely to that of a calcium chlor-aluminate hydrate, $3CaO.Al_2O_3.CaCl_2.10H_2O$, as shown in the following analysis:

	Theoretical composition	From actual analysis
Al_2O_3	18.16	18.44
$3CaO$	29.97	29.67
$CaCl_2$	19.77	19.60
$10H_2O$	32.10	32.30
Total	100.00	100.01

Microscopic examination showed that this chlor-aluminate was composed wholly of crystals as thin hexagonal plates with the following refractive indices: $\omega = 1.550 \pm 0.003$ and $\epsilon = 1.535 \pm 0.003$. The plates were uniaxial negative. The chlor-aluminate from the mixtures of $AlCl_3$ and $Ca(OH)_2$ has essentially the same optical properties, although the indices varied slightly in the different samples, as did those of the tricalcium aluminate previously studied. However, the indices of the latter were in all cases lower than those of the chlor-aluminate.

Calcium chloride was also added to other aluminate solutions containing relatively more alumina (as monocalcium aluminate) and less "free" calcium hydroxide than in the case of the solution used in the experiment just described. Two phases precipitated from such solutions; one a hydrated chlor-aluminate as described above, and the other hydrated alumina similar to that precipitated from the metastable calcium aluminate solutions, and previously described. It was evident from the chemical analyses of the aluminate solutions to which the calcium chloride was added that the "free" calcium hydroxide was insufficient for the sole formation of $3CaO.Al_2O_3.CaCl_2.10H_2O$. It is evident, therefore, that the resultant composition of the precipitate depends upon the composition of aluminate solution as well as upon the total concentration of calcium chloride in the resultant mixture.

Lafuma [67] has prepared a calcium chlor-aluminate of the composition, $3CaO.Al_2O_3.CaCl_2.18H_2O$, by the addition of about 5 per cent NaCl or $CaCl_2$ and 4 g CaO to an aluminate solution, with the subsequent removal of excess CaO by dilution with a 5 per cent NaCl solution until the resulting solution contained about 0.5 g CaO per liter. This formula differs from that of $3CaO.Al_2O_3.CaCl_2.10H_2O$ as previously obtained by Friedel [68] and more recently found in the investigation herein described only in the degree of hydration.

[67] Lafuma, Recherchies sur les aluminates de calcium et sur leurs combinaisons avec le chlorure et le sulfate de calcium. Thèse, Paris, p. 52; 1925.

[68] Bull. Soc. Franc. Mineral. 19, p. 122; 1897.

Poisson [69] concluded that the formula of the calcium chlor-aluminate was $2(3CaO.Al_2O_3).CaCl_2(H_2O)$ or $3CaO.Al_2O_3.0.5CaCl_2(H_2O)$. Lafuma has criticised his work and thinks that Poisson analyzed a partially decomposed chlor-aluminate. Also, from the present work herein described, it appears that Lafuma's criticism is well founded. It is hoped that further investigations may throw more light upon the reactions of the chlor-aluminates.

TABLE 17.—*Showing decrease in pH of aluminate solution as a function of the concentration of chloride*

Total grams chloride per liter	pH of solutions after addition of chlorides					Analyses of solutions before and after addition $MgCl_2$	
	$CaCl_2$	$MgCl_2$	$BaCl_2$	NaCl	NH_4Cl	Al_2O_3 g per l	CaO g per l
0.0	11.52	11.52	11.52	11.52	11.52	0.3435	0.4060
0.5	11.37	10.81					
1.0	11.28	8.98					
2.0	10.97	8.11				None.	.3960
5.0	10.56	7.85				None.	.3900
10.0	10.39	8.11				None.	.3970
20.0	10.05		11.37		7.89	None.	.4010
23.5		7.14					
30.0	9.81			11.27			
50.0	9.84						
50.0	9.78						
50.0	9.80						

TABLE 18.—*Showing the per cent $CaCl_2$ in the calcium chlor-aluminates as a function of the $CaCl_2$ in the mixtures*

Total grams $CaCl_2$ per liter (approximate)	Normality $CaCl_2$ (approximate)	$CaCl_2$ in calcium chlor-aluminate
		Per cent
0.47	[1] 0.0086	13.32
0.5	.0090	13.41
0.6	[1] .0107	14.78
0.72	[1] .0129	15.98
1.0	.018	16.43
2.0	.036	17.35
5.0	.090	16.29
10.0	.180	18.62
20.0	.360	18.06
30.0	.560	19.25
50.0	.901	19.60

[1] From mixtures $AlCl_3$ and $Ca(OH)_2$ (see Table 16).

3. REACTION OF OTHER CHLORIDES ON ALUMINATE SOLUTIONS

An investigation was also made of the effect of barium, magnesium, sodium, and ammonium chlorides upon a calcium aluminate solution. This solution contained 0.3435 g Al_2O_3 and 0.4060 g CaO per liter and had a pH value of 11.52.

Weighed quantities of C. P. magnesium chloride were first added to aliquots of this solution, and later the resultant mixtures were

[69] Ciment, 6, p. 108; 1910.

examined in the manner described in the study of the calcium chlor-aluminates. The addition of increasing quantities of $MgCl_2$ reduced the pH of aluminate solution from 11.52 to 7.14, the successive reductions being in each case lower than those affected by the addition of corresponding amounts of $CaCl_2$. These reductions are recorded in Table 17 and graphically represented in Figure 18. Also, from columns 7 and 8 of Table 17 it may be noted that, although the precipitation of alumina was complete at concentrations of $MgCl_2$ in excess of 2 g per liter at pH values less than 8.11, yet but traces of lime were precipitated, or accluded with the alumina. Apparently little or no calcium chlor-aluminate is precipitated by the addition of this quantity of $MgCl_2$. Whether this compound is formed at concentrations of $MgCl_2$ less than 2 g per liter could not be ascertained, since the precipitate was colloidal and could not be filtered readily. Microscopic examination of the filterable precipitates showed the absence of any crystals which resembled calcium chlor-aluminate.

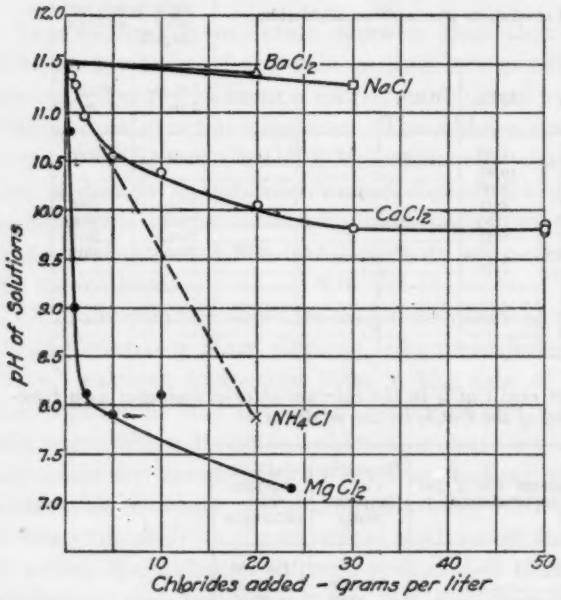

FIG. 18.—*Curves showing the decreases in the pH of an aluminate solution attended by the addition of various chlorides*

The material appeared to be amorphous and was found by chemical analysis to contain both aluminum and magnesium (presumably as hydrated oxides). It was found previously from the electrometric titration of $AlCl_3$ with $Ca(OH)_2$ that hydrated alumina is precipitated from solution as the stable phase at the pH between 7.14 and 8.11, the values attained by the addition of more than 2 g of $MgCl_2$ per liter. Apparently, then, the $MgCl_2$ reacts with the "free" $Ca(OH)_2$ of the aluminate solution to form insoluble magnesium hydroxide, the calcium chloride remaining in solution. The hydroxyl ions are thus removed from the field of action to such an extent that the alumina, which has been in solution as an aluminate, pre-

cipitates also as the hydroxide. The precipitate is thus a mixture of aluminum and magnesium hydroxides.

It was found upon the addition of sodium or barium chloride to the calcium aluminate solution that a small quantity of calcium chlor-aluminate was precipitated gradually and that the pH of the solution was but slightly decreased. This indicates that barium chlor-aluminate is more soluble than calcium chlor-aluminate. It has also been shown that both the concentration of calcium chloride and "free" calcium hydroxide are factors of moment in the precipitation of the calcium chlor-aluminates. This accounts for the small amount of this compound being precipitated, since the quantity of calcium chloride which could be formed by the reaction between the calcium hydroxide and sodium or barium chlorides is too limited. The addition of either $CaCl_2$ or $Ca(OH)_2$ to the mixtures resulted in the formation of increasing amounts of $3CaO.Al_2O_3.CaCl_2.10H_2O$.

Ammonium chloride, on the other hand, reacted more like magnesium chloride on the aluminate solutions. The addition of 2 g NH_4Cl to a liter of the aluminate solution resulted in a decrease in pH from 11.52 to 7.89 with the complete precipitation of the aluminum as the hydroxide. Analysis of the filtrate showed that no calcium was precipitated. The reaction of the ammonium chloride on the calcium aluminate solution may be explained as follows: The ammonium chloride reacts with the calcium hydroxide of the aluminate solutions to form ammonium hydroxide, which is but slightly ionized. The ionization is further represseed by the "common ion effect" of the NH_4^+ of the additional ammonium chloride to such an extent that the hydroxyl-ion concentration becomes sufficiently low to cause the formation of the insoluble aluminum hydroxide. The lime is converted to calcium chloride and remains in solution.

V. SUMMARY

This investigation included the study of the mechanism of the reaction of water on a high alumina cement and the following anhydrous calcium aluminates: Monocalcium aluminate, 3:5 calcium aluminate, 5:3 calcium aluminate, and tricalcium aluminate.

Since the addition of water to tricalcium aluminate, $3CaO.Al_2O_3$, produces a very vigorous reaction, the changes in the composition of the resulting aqueous solutions could not be followed in the case of this aluminate. Previous investigations have indicated that its setting is due to the formation of hydrated tricalcium aluminate.

On the other hand, since the activity of the other aluminates and high alumina cement toward water is distinctly less than that shown

by the tricalcium aluminate, it was possible to follow the mechanism of the reaction in the formation and decomposition of the metastable calcium aluminate solutions. During the early periods of the reaction a portion of the line and alumina in each case passed into solution as the calcium salt of monobasic aluminic acid. The total concentration of this aluminate depended upon the chemical composition of the anhydrous aluminate or cement from which it was formed, as well as upon the time of reaction. However, these monocalcium aluminate solutions were metastable and soon decomposed with precipitation of a portion of the lime and alumina. The molar ratio of the lime to the alumina remaining in solution after precipitation increased and was attended in each case by an increase in the pH from about 11.1 to 11.75.

Identical changes in the metastable solutions took place when filtered from the reaction mixture. Part of the lime and alumina likewise precipitated from these clear metastable solutions and resulted in "equilibrium" solutions similar to those obtained when the aluminate or high alumina cement had been left in contact with the water for long periods. In both cases equilibrium apparently was reached only after several weeks had elapsed.

Chemical analyses and microscopic examinations of the material precipitated from the metastable solutions indicated that hydrated alumina and hydrated tricalcium aluminate were precipitated as equilibrium was approached. The pH of the aqueous solution in equilibrium with these two solid phases, hydrated alumina and hydrated tricalcium aluminate, is approximately 11.75.

The constitution of the aluminates in solution was reviewed in the light of previous investigations, where it has been shown that aluminum hydroxide is an amphoteric electrolyte and, as an acid, is primarily monobasic. Calculations based upon electrometric measurements and chemical analyses are submitted which indicate that the alumina exists in solution as the calcium salt of monobasic aluminic acid, and that the quantity of "free" calcium hydroxide in excess of this salt is the determining factor of the pH. The conclusion of Slade, Blum, and Heyrovsky that aluminic acid is a relatively strong monobasic acid has been confirmed.

It has been shown that the more concentrated monocalcium aluminate solutions are metastable, since they are supersaturated with respect to the more insoluble form of aluminic acid (hydrated alumina) as well as to the hydrated tricalcium aluminate.

An investigation has been made of the subsequent changes in the aluminate solutions attended by increasing concentrations of calcium hydroxide. As the concentration of calcium hydroxide is increased, increasing proportions of the total alumina are precipitated, until at a pH of 12.0 or above the alumina is completely precipitated from

solution. Some lime is also precipitated with the alumina. The molar ratio, lime to alumina in the precipitated material, increases with an increase in pH. A tetracalcium aluminate of the composition, $4CaO.Al_2O_3.12H_2O$, appears to be formed at a pH above 12.0.

Analogous changes in the aluminate solutions are affected by the calcium hydroxide liberated by the hydrolysis of tricalcium silicate in such solutions. The hydrolysis of beta dicalcium silicate appears to be greatly inhibited by an aluminate solution.

A study of the electrometric titration of $AlCl_3$ with $Ca(OH)_2$ has been made. The precipitation of aluminum as the hydroxide is complete between pH 6.0 and 7.5, a confirmation of the conclusions of Blum. Appreciable resolution of the aluminum hydroxide occurs in solutions in which the pH is greater than 9.0. The alumina redissolves completely at a pH of 10.9. At the higher alkalinities a calcium chlor-aluminate is formed. This aluminate may also be prepared by the reaction of calcium chloride on an aluminate solution; its chemical composition depends upon the composition of the aluminate solution and the concentration of calcium chloride. If the concentration of the latter exceeds 3 per cent, the composition of the chlor-aluminate approaches $3CaO.Al_2O_3.CaCl_2.10H_2O$. The optical properties of this compound have been determined.

Barium chlor-aluminate appears to be more soluble than calcium chlor-aluminate. Ammonium chloride and magnesium chloride both decompose calcium aluminate solutions, with the precipitation of aluminum hydroxide by the ammonium chloride and of a mixture of aluminum and magnesium hydroxides by the magnesium chloride.

In carrying out the work in connection with this paper the author has had the assistance of W. Lerch in the preparation of the anhydrous calcium aluminates and silicates, and Dr. H. Insley in the petrographic examination and preparation of photomicrographs of the products of hydration. Thanks are also expressed to other members of the bureau staff for all assistance given, especially to L. A. Palmer for his excellent suggestions and criticism in the preparation of this manuscript, and to P. H. Bates for his great interest and valuable assistance in the progress of this research.

WASHINGTON, June 1, 1928.

UNIDIRECTIONAL RADIOBEACON FOR AIRCRAFT

By E. Z. Stowell

ABSTRACT

A method of transmitting unidirectional beacon signals for the aural or visual guidance of aircraft has been worked out. Such signals increase the efficiency of the beacon from the power standpoint, reduce interference from other beacons, and reduce the number of radiated courses to one. It is believed that the polar characteristic of the radiated field is about the optimum for aircraft use.

The method consists in transmitting directive and nondirective fields simultaneously, with the proper phase and amplitude relations between them to secure unidirectional transmission.

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I. INTRODUCTION

During the development by the Bureau of Standards of a directive beacon for guiding aircraft[1] it appeared that the usefulness of the beacon could be increased by making the radiated field unidirectional. As the operation of a considerable number of beacons was contemplated, all on the same frequency of 290 kc (1,034 m), a large amount of the interference between them might be prevented in this way. In addition, more signal intensity might be obtained in a desired direction with a given amount of power, and the pilot would be less subject to confusion from a multiplicity of possible courses.

These considerations had sufficient weight to warrant experimentation. The attempts to obtain such a unidirectional arrangement without seriously departing from the directive beacon circuits as they then stood are described in this paper.

II. PRINCIPLE OF THE DIRECTIVE BEACON

The beacon system, without the unidirectional feature, has been fully described.[1] The principles involved will be briefly stated here.

[1] Development of radio aids to air navigation, J. H. Dellinger and H. Pratt, Proc. I. R. E., 16, pp. 890-920, July, 1928.

Figure 1 shows a schematic diagram of the arrangement. A master oscillator supplies power at 290 kc to two power-amplifier tubes. These operate alternately, say with a 500-cycle plate supply. In the plate circuits are the stator coils of a goniometer, the secondaries of which are in series with their respective coil antennas at right angles.

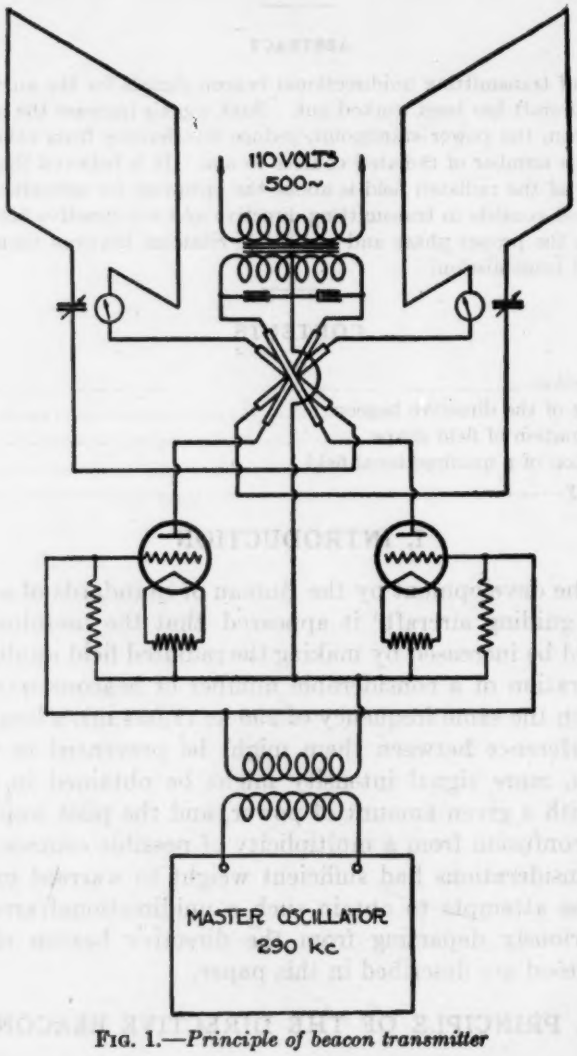

FIG. 1.—*Principle of beacon transmitter*

It can be demonstrated that the resultant signal is that emitted by two radiating loops (coil antennas), the size of the actual loops used, but inclined to each other by the angle between the stator coils of the goniometer, and whose apparent orientation can be shifted by rotating the goniometer coils (either pair). These equivalent loops are some-

times called the "phantom loops" to distinguish them from the physical loops carrying the power to be radiated.

Given a fundamental circuit arrangement of this kind, a number of ways can be found to make the modulation mark out lines in space which radiate from the transmitter like the spokes of a wheel. For example, in the above system there will be four directions from the transmitter in which a 1,000-cycle note will be emitted. These are the directions in which the signals from the two phantom loops are received with equal intensity. These directions are theoretically lines, or zones of no width, but they actually have a small width depending on the discrimination of the receiving operator or receiving equipment. Hence, these directions are generally referred to as equisignal zones.

In all other directions the received note will be 500 cycles. Since these four directions 90° apart can be swung around in space together, we have a flexible system for indicating a desired direction to an airplane. In practice such a system would be useless, for it would be quite difficult for an airplane which accidentally wandered off this course to find it again. It turns out that an additional feature must be provided which informs the airplane which side of the course is right and which is left. This feature does not concern the present paper, and it is only necessary to state that if the above fundamental system can be gotten to radiate a unidirectional field, the modifications necessary to insure practical working with an airplane follow naturally. Accordingly, most of the experimental work was done with the above arrangement.

III. DETERMINATION OF FIELD SHAPE

A single loop radiates a figure of eight because of the phase interference from the parallel sides. Two loops sending alternately would, therefore, radiate two figures of eight inclined to one another by the angle between the loops. In the case of the beacon transmitter of Section II, if the primary coils of the goniometer are placed at 60°, the emitted field is that of two loops at 60°, shown in Figure 2 (*a*). If the coils are at right angles, the field is that of Figure 2 (*b*).

In case the alternations from one loop to another are sufficiently rapid, the detecting device can not follow them, and the two fields overlap to give the resultant fields in these figures. Such is the case, for example, with 500-cycle plate supply at the transmitter and a thermoelement at the receiving end. Since most reception devices would integrate the signal in this manner, the measurements of field shape were made upon the "resultant fields," generally with a thermoelement at the output of a receiving set, sometimes with a 2-electrode detector feeding a Leeds & Northrup automatic recorder.

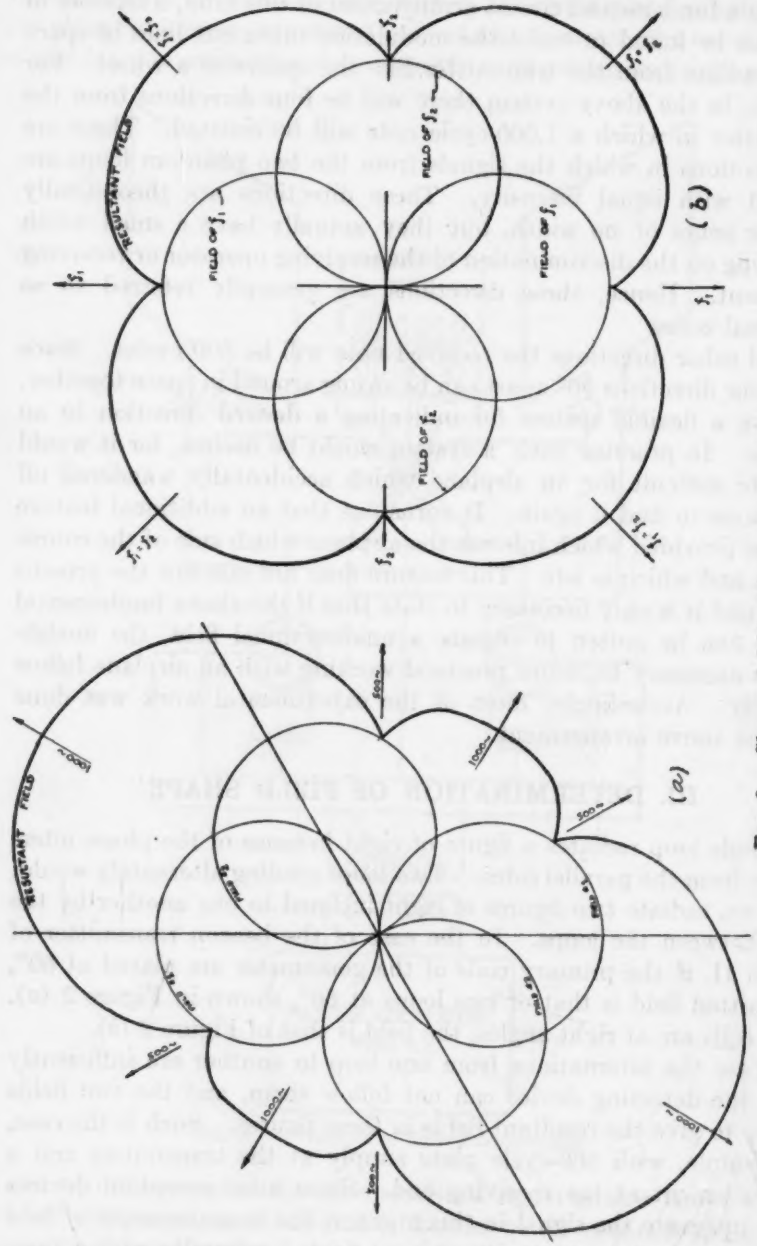

FIG. 2.—*Shape of field of beacon transmitter*

a, with goniometer stators (phantom loops) at 60°
b, with goniometer stators (phantom loops) at 90°

IV. PRODUCTION OF A UNIDIRECTIONAL FIELD

Methods of transmitting unidirectional signals fall into two broad classes. One employs the antenna array and is probably the most widely used. It consists of a number of antennas appropriately spaced and excited at the proper times from the same source. Quite varied fields have been gotten in this manner, which have been discussed in the literature.[2] These methods are open to two objections for the purpose of the present beacon—the amount of land necessary might be excessive and the design is radically different from the beacon as already developed. However, a beacon operating in one of the high-frequency bands might be economically constructed on this principle.

The second group of methods approaches more nearly the needs of the present beacon. This group is characterized by the superposition of a nondirectional field upon a bilateral field (such as a figure of eight) to produce a unilateral field (such as a cardioid). This was first done by Bellini and Tosi.[3] They employed two triangular loops at right angles, open at the top, and excited from a goniometer. A single vertical wire was supplied with power from an extra winding on the goniometer that supplied the loops. By adjusting phase and amplitude relations between the directive and nondirective fields a cardioid could be radiated in the most favorable case. This was proved by reception measurements. The cardioid could be oriented in any direction by rotating the goniometer.

With this as a clue, experiments were made upon the beacon at College Park, Md., with a vertical wire 70 feet long, radiating simultaneously with the loops. Various methods of feeding were tried, the circuit arrangement of Figure 3 giving best results. Figure 4 shows the shape of the field as received on an automatic recorder at the Bureau of Standards, 11 miles distant, while the goniometer was rotated at a constant rate. The dip at 270° shows the effect of the vertical wire. The effect is not very pronounced, due to lack of power in the wire. The wire was tuned by loading it with a variometer; hence, the currents in the wire and the loops are in phase or nearly so.

In order to increase the effect of the nondirective field, it became necessary to use a more efficient radiator. Such a radiator was already at hand in the loop structure. (See fig. 5.) The connection

[2] F. Braun, Electrician, **57**, pp. 222 et seq., 244 et seq.; 1906. Bellini, Electrician, **74**, p. 352; 1914. R. M. Foster, Bell System Tech. J., **5**, p. 292; April, 1926. Blondel, Compt. Rend., **184**, pp. 561, 721; 1927. Richtcharakteristiken von Antennenkombinationen, by A. Esau, Jahrb. d. drahtl. Tel. und Tel., **27**, pp. 28, 142; 1926 (in 3 parts). Directive transmission with grid antennas, Meany, L'Onde Electrique, **6**, p. 181; 1927. Approximate theory of the flat projector (Franklin) aerial used in the Marconi beam system of wireless telegraphy, J. A. Fleming, Exp. Wireless, **4**, p. 287; 1927.

[3] Bellini and Tosi, A directive system of wireless telegraphy, Electrician, pp. 62, 531; 1909. Murphy and Wolfe, Stationary and rotating equisignal beacons, J. Soc. Auto. Engrs.; September, 1926.

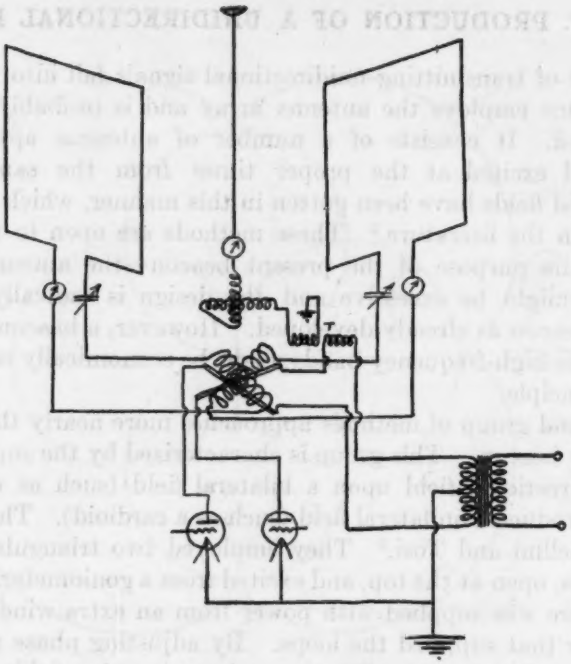

FIG. 3.—*Excitation of vertical wire from goniometer circuit*

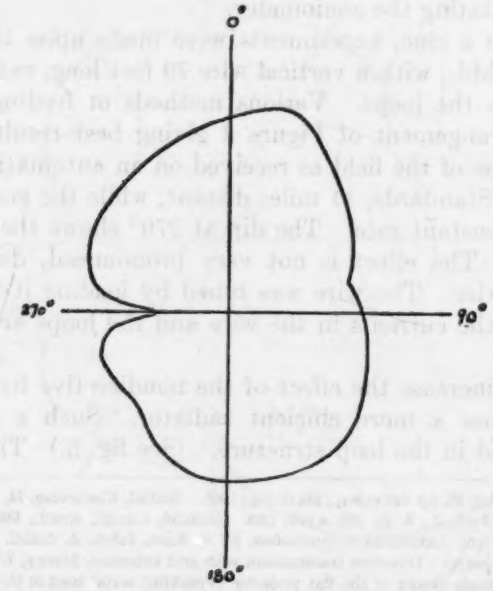

FIG. 4.—*Field of loops and vertical wire*

FIG. 5.—*Antennas of experimental beacon at College Park, Md.*

to the vertical wire was replaced by a connection to the common mid-point of the loops as in Figure 6.

This connection was without effect on the circulating currents in the loop themselves; that is, the loops could be connected together at their mid-points and grounded without changing the readings of the ammeters in series with the loops. The increased effectiveness is shown by the fact that in Figure 6 the ammeter in series with the variometer registered 3 to 5 amperes with the power available, as against 1 ampere with the connection of Figure 3.

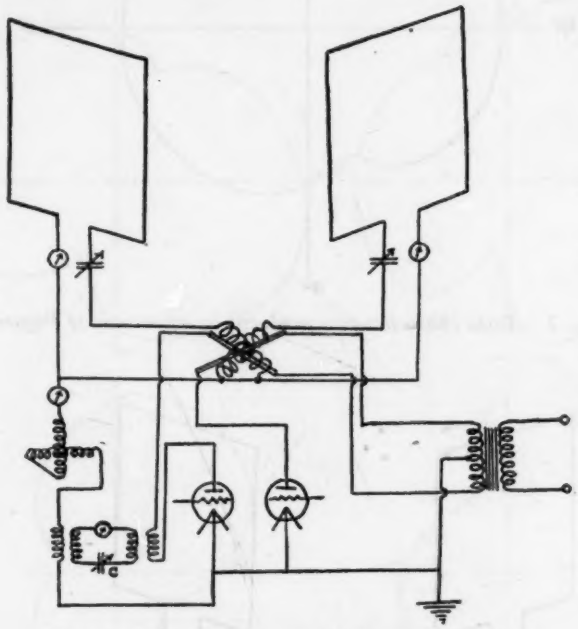

FIG. 6.—*Use of loops as simultaneous radiators of directive and nondirective fields*

The field resulting from this circuit arrangement is shown in Figure 7. This disappointing result led to an examination of the transfer of power to the variometer circuit. It was found that the majority of the power was being transferred capacitively through the transformer and that instead of the nondirective field being in phase with the directive field, it was close to 90° ahead in time. Therefore, a delay circuit was interposed between the variometer circuit and the power source, as in Figure 8, to bring the two fields more nearly in phase. The improvement is seen in Figure 9 (*a*), (*b*), (*c*), and (*d*), taken with progressively increasing nondirective fields. It is evident that none of these fields are sufficiently unidirectional for practical use. The back radiation from Figure 9 (*d*),

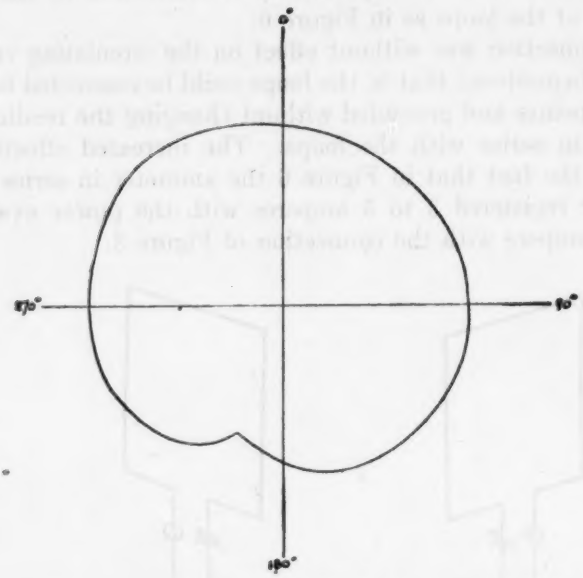

FIG. 7.—*Field characteristics produced by apparatus of Figure 6*

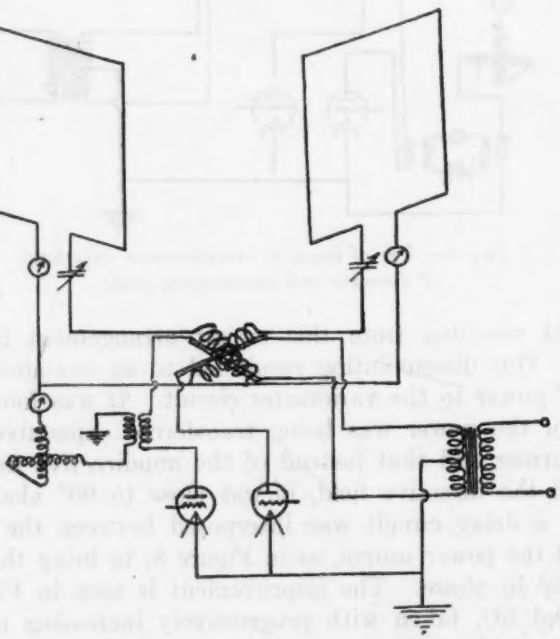

FIG. 8.—*Same as Figure 6 with delay circuit*

for example, is still sufficient to give a powerful audible signal or to operate a sensitive indicator.

The circuit arrangement which finally gave the desired result is shown in Figure 10. The power for the nondirective field is obtained from an auxiliary goniometer whose primary windings are at 90°, and in series with the primaries of the goniometer controlling direction. Both goniometers were wound to minimize capacity transfer between windings. Hence, the phase of the nondirective field should be accurately controllable with the variometer, and a considerable

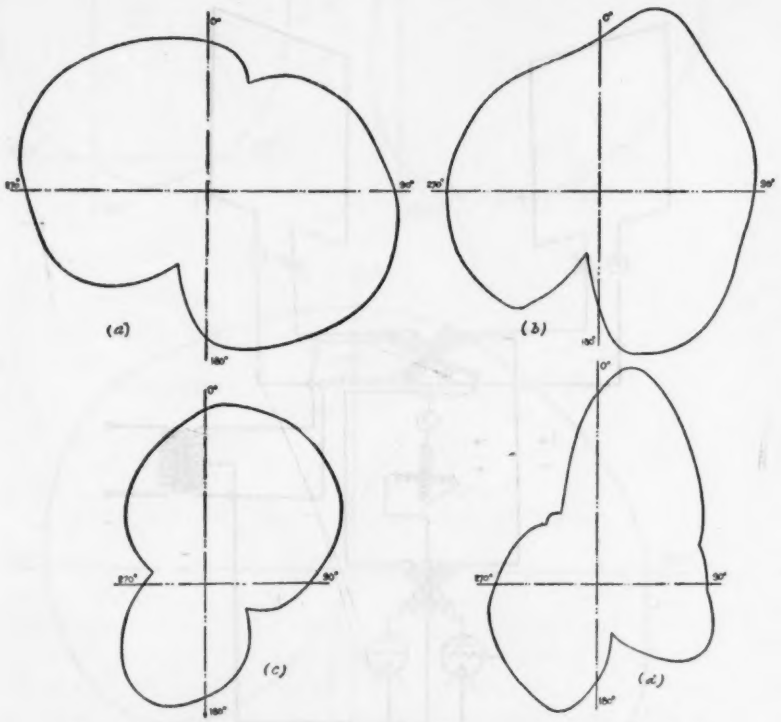

FIG. 9.—*Field characteristics produced by apparatus of Figure 8*

variation in amplitude is obtainable by change of the primary turns of the goniometer. By independent adjustment of these two, the appropriate phase and amplitude of the nondirective field with reference to the directive field, was found. A unidirectional field is obtained with the current 55° different in phase one way or the other from the loop currents. Figure 11 (*a*) shows the field with the nondirective field 55° ahead of the directive field; Figure 11 (*b*) with the nondirective field 55° behind the directive field. With intermediate phase displacements, fields like Figure 11 (*c*) are obtained. The fields of Figure 11 (*a*) and (*b*) can be rotated by means of the

goniometer which normally controls the direction, leaving the remainder of the circuit unchanged during the rotation. This was proven by receiving the field at two locations, and checking the displacement of the maximum on the goniometer scale.

Since the marking out of courses is accomplished with modulations, such a polar field is useless unless the modulations retain their ability to form a sharp equisignal zone as explained in Section II. That they do is proved by directing the maximum of the polar field, say of Figure 11 (*a*), at an observer, and adjusting the position of the sec-

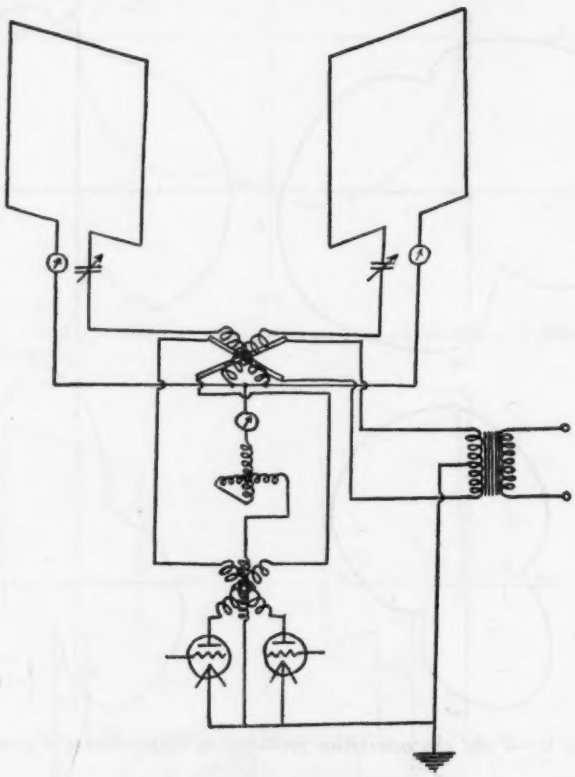

FIG. 10.—*Final circuit arrangement*

ondary of the auxiliary goniometer until the equisignal zone appears. This may be manifested audibly by the rise of an octave in pitch of the received note, or visually by proper operation of a course indicator. Under this condition, the most useful signal coincides in space with the maximum signal.

In Figure 11 (*a*) and (*b*), the arrows represent the angular position of the centers of the equisignal zones. It is seen that Figure 11 (*a*) has but one radiated course instead of the usual four, and it occurs

practically at the maximum of the field. Figure 11 (*b*), while possessing an excellent polar characteristic, is not so acceptable from the standpoint of radiating useful signals. Two courses are radiated,

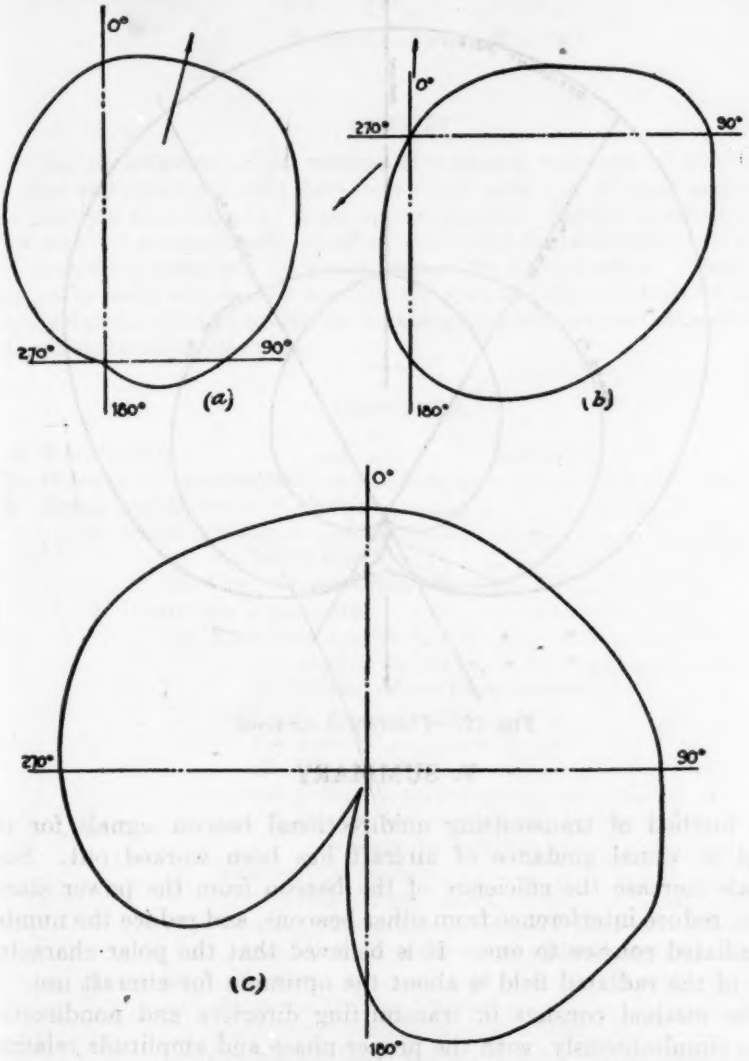

FIG. 11

a, Field at bureau, *L* subtracted
b, Field at bureau, *L* added
c, Field with wrong phase displacement

both very weak. Figure 11 (*c*) is out of the question, both from the standpoint of the polar field and of the useful signal.

A "beam" for airplane reception must not be too narrow in order that the airplane may find it without too much difficulty. If it is

too broad, the unidirectional effect is lost. It is believed that the fields of Figure 11 (*a*) and (*b*) represent about the optimum for airplane use.

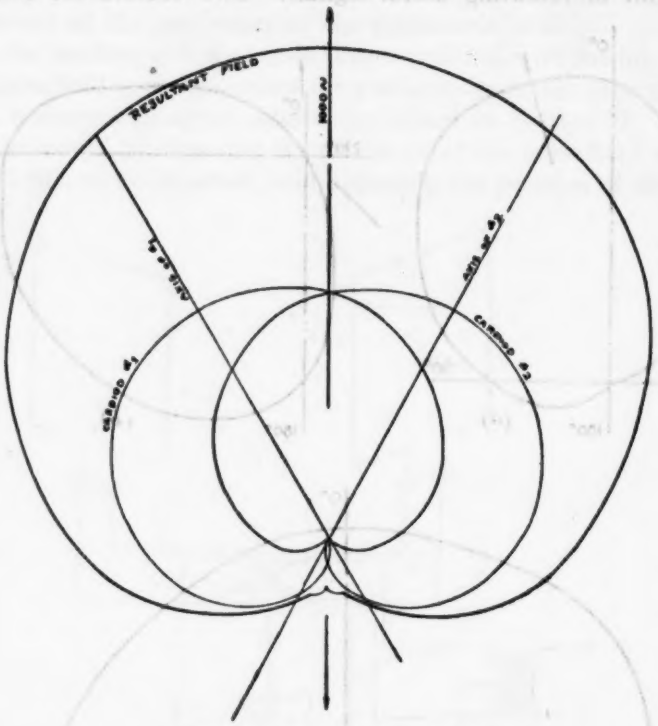

FIG. 12.—*Theoretical cardioid*

V. SUMMARY

A method of transmitting unidirectional beacon signals for the aural or visual guidance of aircraft has been worked out. Such signals increase the efficiency of the beacon from the power standpoint, reduce interference from other beacons, and reduce the number of radiated courses to one. It is believed that the polar characteristic of the radiated field is about the optimum for aircraft use.

The method consists in transmitting directive and nondirective fields simultaneously, with the proper phase and amplitude relations between them to secure unidirectional transmission.

Acknowledgments are due the American Telephone & Telegraph Co. for the use of a private line connecting the beacon with two receiving locations in Washington; and to F. M. Baer, of the bureau's radio section, for valuable assistance in making the observations.

WASHINGTON, January 21, 1928.

STUDIES OF MACHINES FOR EXTRUDING CLAY COLUMNS

AUGERS, SPACERS, AND DIES FOR BRICK MACHINES

By Paul C. Grunwell

ABSTRACT

In this investigation special mechanical apparatus was designed and built to measure and record the work done on a known weight of extruded material by any practical combination of auger, spacer, and die. Electric metering devices were modified to compensate for current difficulties in the electric-power service and to measure accurately the power input to the auger machine. Means were devised to make comparisons between the workable characteristics of various clays and shales and for selecting the extruding equipment to mold them efficiently into suitable commercial forms.

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I. INTRODUCTION

Practically no fundamental data are available as a basis for the intelligent design and operation of continuous extrusion machines used for molding plastic materials. This is especially true of auger machines used for molding clays in the process of making stiff-mud bricks, hollow blocks, and similar products.

The inventor (58)[1] of the first successful auger brick machine used in America was granted letters patent in 1863. This machine produced a continuous bar or column of clay by extrusion from a die opening, the propelling force being supplied by a rotating auger; hence the name "auger machine."

This machine was the forerunner of the present auger machines in which the same original principles of barrel, die, and rotating auger are present as were incorporated in its predecessor. The improvements which have been made, in the absence of fundamental data, have resulted mostly from "cut-and-try" methods through cooperation between machine builder and machine user. The principal improvements made to date have been toward increasing the size and capacity of the machine to meet present-day demands for greater production.

The urgent need for reliable data to improve the design and operation of auger machines was emphasized at a conference of Government and industrial representatives in the fall of 1923. As a result of this conference, the Bureau of Standards undertook a study of the design factors pertaining to augers, spacers, and dies for extrusion machines.

[1] The figures in parentheses here and throughout the text relate to the numbered references in the bibliography at the end of this paper.

Considerable experimental work of general interest has been done by various clay-equipment firms and private individuals in the production field, but no fundamental laws of design or operation have been developed. This made it necessary to do considerable pioneer work in practically all phases of this investigation. Individual features in the development of the extrusion machine have been worked out to meet particular requirements of certain manufacturers of clay wares, and are therefore of limited value to others whose problems or clays are different. Nevertheless, the combination of the best features resulting from such experience has been the guiding influence enabling the equipment builder to develop the auger machines in use at the present time.

Certain inherent difficulties have always attended the use of extrusion machines for the manufacture of heavy-clay products, such as the development of uneven stresses and column defects in the molding operation. Many attempts have been made to overcome the defects which are present to a greater or less degree in brick and hollow ware made by the auger machine. These defects, however, depend to some extent upon the nature of the clay used. It appears that certain types of clay work better with certain forms of augers than with others when combined with a die of a certain length and taper. A proper die for very plastic clay may not work as satisfactorily with the same auger for a lean clay. So far the method of "cut-and-try" has been the principal means of finding out what combinations of auger, spacer, and die will work a particular type of clay most satisfactorily. Very little experimental work has been done on the extrusion machine as a whole, but considerable work has been done on the flow of plastic materials through dies, principally by Artz (11), Morris (26), Brand (30), Stull (36), and others.

The physical properties of the clays and shales found in different parts of the country or even in the same locality are so vastly different that many combinations of types of augers and dies are necessary in order to successfully mold the different shales and clays into desired shapes by the extrusion process. It is also known that column speed is materially affected by the length and taper of the cone-shaped nozzle or approach to the die and that excessive taper causes excessive differential flow and greater resulting friction. This increased friction has its advantages, however, in knitting spirals and cleavages in the clay caused by the rotation of the auger. The principal determining factors regarding the proper distance between the die and the auger tip are: (1) Uneven flow of material, (2) torn corners, (3) cracked column, and (4) equalization of pressure back of the die. The temper of the clay must be regulated to the proper degree and sufficient "flow resistance" must be provided; other-

wise the clay will not have sufficient pressure to fill the die and form a perfect column. Any plastic clay in the stiff-mud state may be made to flow through a die if sufficient pressure is applied, but the important problem is to determine what the design factors are that contribute to the perfection of the clay column and at the same time to determine what effect these have on power consumption.

In the following work methods have been devised for isolating and studying the causes of these difficulties, with a view to determining what the design factors are that control or govern them and to obtain data upon which to base fundamental design specifications. Several preliminary runs were made using brick and hollow-tile dies, preparatory to arranging a schedule of tests on types of augers, different lengths and tapers of dies, and various lengths of collective spacers, comprising approximately 300 extrusion tests, 1,400 flow tests, and 4,000 moisture determinations. The study of the performance of augers, dies, and collective spacers has been accomplished by eliminating as many of the above-mentioned variables as possible and then correlating the remaining variables in such a manner as to single out the performance of each auger, die, and collective spacer.

Other laboratory tests were made simultaneously with the extrusion tests to determine the water content for best workability of the material by the use of a separate piece of apparatus called a flow cylinder and a special constant-speed testing machine. The workability of the material is indicated by the pressure in pounds per square inch required to produce flow through a ½-inch-diameter orifice and is hereinafter referred to as "flow pressure."

To facilitate in maintaining the moisture in the material within suitable limits a moisture-proof chamber was constructed of about 2 tons capacity, in which the tempered material was stored ready for use.

In addition to the laboratory work, the available literature and Patent Office records dealing with the development of auger machines and dies during the past 60 years have been reviewed.

II. SCOPE OF THE INVESTIGATION

This investigation embodies a study of the fundamental principles employed by the trade in the formation of a clay column by means of mechanically forcing plastic clay through a die with a rotating auger. The major considerations of this part of the investigation comprise a study of the design factors of augers, spacers, and dies and the types best suited to the physical characteristics of the clay or shale with which the tests were made.

Although the problem of laminations has not been seriously considered in this part of the investigation, the tendency of the various designs of augers and dies to increase or eliminate auger and die

laminations has been noted. The principal studies entering into this section of the investigation are:

1. A study of the tempering and molding properties of several clays and the selection of one suitable for repeated use in making extrusion tests.

2. Determination of the proper amount of water to be added in tempering the clays and shales used in the tests in order to obtain the most stable working conditions.

3. Effect of moisture change and effect of repeated extrusion on the workability of the tempered material.

4. Power consumption, production, and quality of the product, depending upon the following:

A. Performance and relative efficiency of augers.

B. Effect of the distance of the ingress of the die from the auger tip (hereinafter referred to as the collective space).

C. Effect of die length.

D. Effect of die lubrication.

In addition to the usual ceramic-laboratory apparatus, the equipment used consists of a 2,000-pound capacity testing machine; a stiff-mud auger machine of a typical design; single, double, and triple wing augers; 6, 8, and 10 inch lengths of 1° taper standard brick dies; an 8-inch length of 4° taper, metal-lined, wooden die; electric indicating and recording instruments for measuring the electric-power input to the auger machine; specially designed apparatus for measuring the pressure required to produce flow in the tempered materials and the actual power consumed by various types of augers, dies, and spacers; also attachments for measuring the speed, volume, and weight of the extruded materials.

III. DESIGN AND OPERATION OF PLANT

1. DESIGN CONDITIONS

(*a*) Method of Attack.—The extrusion machine used requires a maximum of approximately 45 horsepower at full capacity when working a stiff-mud mixture. It was evident from the start that it would be necessary to deal with a considerable amount of power in the matter of designing a dynamometer to absorb and measure the load. Several methods of attack were carefully considered. In one of these it was proposed to obtain data for an efficiency curve by extending a small shaft through a specially constructed thrust bearing at the end of the auger shaft so as to install a Prony brake and dynamometer. By this means a known load could be imposed in addition to the gross power required to operate the machine when extruding the clay and overcoming the friction losses of the machine. By varying the imposed load a known amount and noting the changes

in the gross power input it would be possible to obtain data for plotting efficiency curves with kilowatt-hours input as abscissae and per cent efficiency as ordinates. This was abandoned because of the difficulty in maintaining a constant load on the auger machine long enough to apply a brake load and obtain accurate readings and also on account of the expense and design difficulties involved in attaching a Prony brake of sufficient capacity to absorb loads varying from 15 to 20 horsepower.

Another method considered was to key an arm and a sleeve to the auger shaft so that the main-shaft gear would be free to rotate and compress a torsion spring which would show by a graduated segment the torque exerted on the auger shaft. This was also abandoned due to design difficulties, such as slow auger-shaft speed and vibrations.

The dynamometer method finally adopted was developed and designed by the investigator. The device which measures the useful work done by the auger and die directly in foot-pounds has proved very satisfactory as to accuracy and reliability. The measuring and registering elements are inclosed in dust-proof housings mounted on solid foundations independent of those for the auger machine and located several feet away. This type of design makes it possible to eliminate most of the vibrations of the auger machine that could not be overcome by the torsion spring or differential-type dynamometer.

The original design of the auger machine used employed a plain thrust bearing for the auger shaft. (Fig. 1.) To eliminate variable friction losses from the measurement of the useful work done by the auger, it was necessary to replace the plain bearing with a tapered-roller thrust bearing. In calculating the maximum thrust of the auger shaft for design purposes and for reference, the following auger-machine dimensions are given:

Diameter of single-thread impeller screw (see fig. 2 at *J*)	inches	13.50
Pitch of single-thread impeller screw	do	8.00
Angle of single-thread impeller screw		10° 35′
The last 8 inches of impeller screw adjacent to the triple-threaded auger tip is tapered down to a diameter of	inches	13.00
Diameter of the tip section adjacent to the impeller screw (see fig. 2 at *M*)	inches	12.50
Diameter of the tip section at the delivering blades	do	11.25
Pitch of each thread on the tip section of the auger	do	13.125

(*b*) CALCULATING THE AUGER THRUST.—The following values were obtained by measurements during preliminary experiments:

Speed of motor, 1,200 r. p. m.; maximum h. p., 45.

Speed of auger, 35 r. p. m.

Power loss through machine to auger by actual test, 13½ h. p.

45 − 13½ = 31½ effective horsepower causing the auger to rotate.

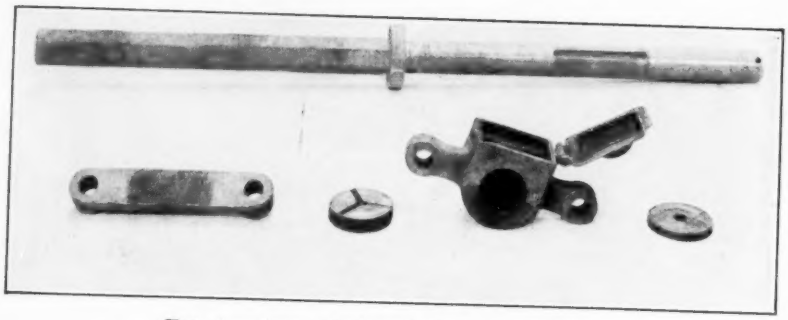
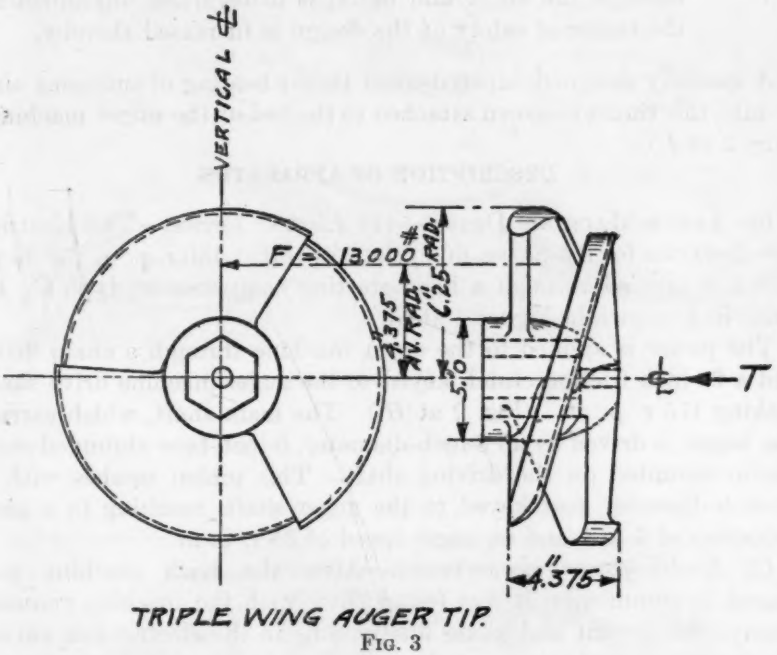


FIG. 1.—*Auger shaft and plain thrust bearing*

FIG. 2.—*Auger machine (partly dismantled) and motor drive*

Let F = a force such that, when applied perpendicularly to a plane passing through the central axis of the auger at a distance from this central axis equal to the radius of the pitch line of the auger thread, it would produce a resistance to turning equal to that produced by the clay when being extruded. The radius of the pitch line of the screw is shown in Figure 3 as 4.375 inches.

Let W = work performed per minute in foot-pounds, then $\frac{W}{33{,}000}$ = h. p. consumed.



TRIPLE WING AUGER TIP.

FIG. 3

Let V = velocity of the point of application of F, in feet per minute.
$= 2\pi \times$ rad. in feet, $\times$ r. p. m.

Then $W = FV = 2\pi \times 0.364 \text{ feet} \times 35 \times F$

$$HP = \frac{W}{33{,}000} = \frac{2\pi \times 0.364 \text{ feet} \times 35 \times F}{33{,}000} = 31.5 \text{ h. p. (as previously stated).}$$

Hence $F = \frac{31.5 \times 33{,}000}{6.28 \times 0.364 \times 35} = 13{,}000$ pounds.

Let T = the calculated thrust from the auger.

Let p = the pitch of the thread on the auger.
= 13.125 inches.

r = the radius of the pitch line of the screw, 4.375 inches, as before.

Since the mechanics of the action of a screw is the same as for an inclined plane whose base is $=2\pi r$ and whose altitude is equal to the pitch, "p," we have the proportion

$F : T = p : 2\pi r$

$$T = \frac{2\pi r \times F}{p} = \frac{6.28 \times 4.375 \text{ inches} \times 13{,}000}{13.125 \text{ inches}}$$

$T = 27{,}250$ pounds, approximate thrust on the plain bearing shown in Figure 1. The power lost due to the propeller blades cutting through the clay and the friction of the clay sliding through the auger and barrel is disregarded, inasmuch as the factor of safety of the design is increased thereby.

A specially designed tapered-roller thrust bearing of sufficient size to take this thrust is shown attached to the bed of the auger machine. (Fig. 2 at *I*.)

2. DESCRIPTION OF APPARATUS

(*a*) AUGER-MACHINE DRIVE.—(1) *Electric service.*—The electric-power service for a 3-phase, 60-cycle, 220-volt, 1,150 r. p. m., 30 h. p. motor is applied through a hand-starting compensator, type C. R. 5025–R–1, shown in Figure 2 at *G*.

The power is applied to the auger machine through a chain drive and a 24-inch friction clutch keyed to the auger-machine drive shaft making 175 r. p. m. (Fig. 2 at *H*.) The main shaft, which carries the auger, is driven by an 8-inch-diameter, 6-inch-face shrouded steel pinion mounted on the driving shaft. This pinion meshes with a 40-inch-diameter gear keyed to the auger shaft, resulting in a gear reduction of 5 to 1 and an auger speed of 35 r. p. m.

(2) *Electric-power measurement.*—After the brick machine was placed in commission it was found that, with the machine running empty, the current and phase fluctuations in the electric line varied the power consumption as much as 5½ h. p. in a period of 20 minutes or less. To overcome the fluctuating conditions of current and phase in the line supplying power to the laboratory, a modified integrating switchboard-type kw.-hour meter was installed (see fig. 2 at *N*) which would integrate the power delivered to the motor, irrespective of the current and phase fluctuations of the line. The recording mechanism of the meter was replaced by a graduated dial mounted on a shaft geared direct to the armature spindle, so that the total revolutions of the armature could be counted and the actual power consumed over any given period of time calculated. After calibration it was possible to measure the actual power consumed by the auger machine to within 1 per cent with this instrument.

(*b*) AUGER-MACHINE EQUIPMENT.—(1) *Augers.*—The term "auger" as herein used refers to all of the revolving element of the auger

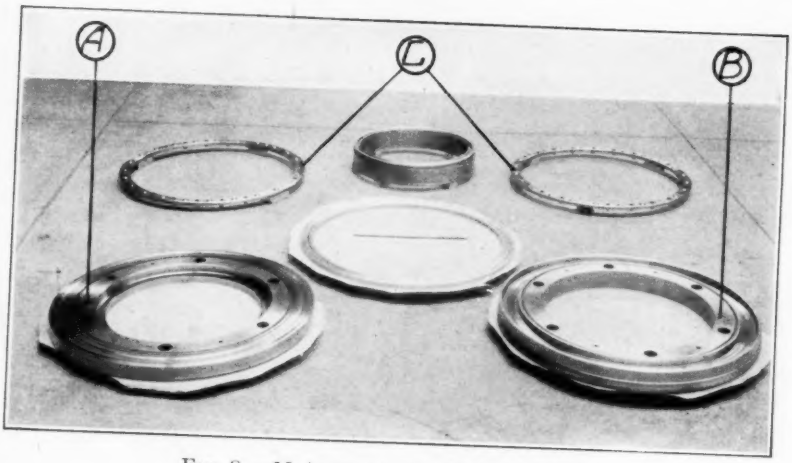


FIG. 8.—*Major parts of ball-bearing joint*

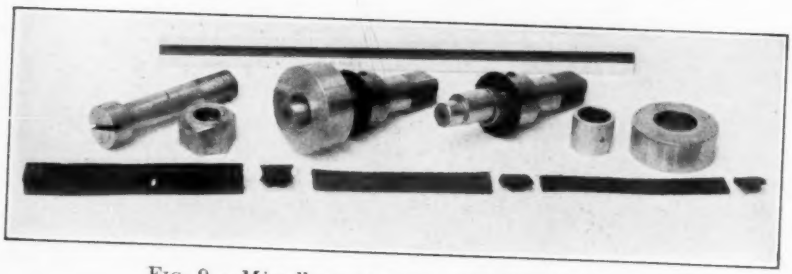


FIG. 9.—*Miscellaneous parts of ball-bearing joint*

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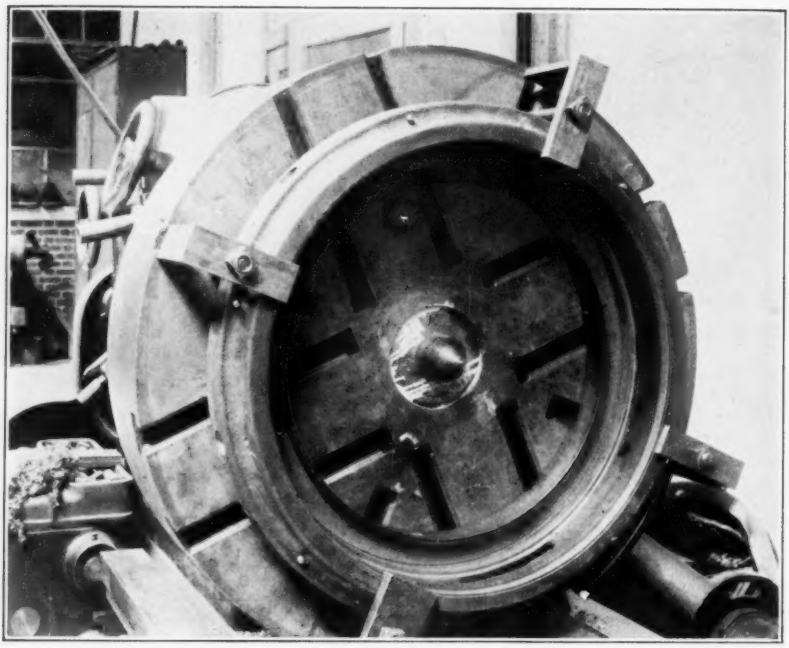

FIG. 10.—*Housing for ball-bearing joint (in process of machining)*

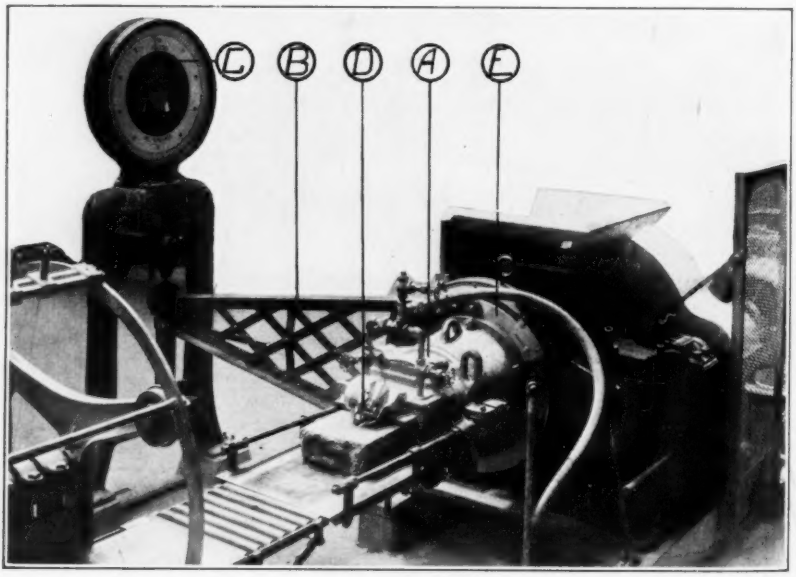

FIG. 11.—*Ball-bearing joint installation* (E)

machine contained in the auger barrel (fig. 2 at *J*), and consists of three impeller blades 13½ inches in diameter, with four beaded-edge half wings 13½ inches in diameter, and one of the three designs of auger tips, as follows:

One single-wing 6-inch pitch, beaded-edge, tapered auger tip, 11 inches long; large diameter 13 inches, small diameter 11 inches. (Fig. 2 at *K*.)

One double-wing beaded-edge auger tip, 11 inches long; large diameter 13 inches, small diameter 10¾ inches. The first turn, or 360°, of thread on the large diameter has a 5-inch pitch; the pitch of the remaining one-fourth turn of the two threads on the small diameter increases from 5 inches at the back to 7 inches at the front or tip of the auger. (Fig. 2 at *L*.)

One triple-wing 13⅛-inch pitch (or 4⅜ inches between centers of successive wings), beaded-edge auger tip, 5¼ inches long; large diameter 12½ inches, small diameter 11¼ inches. (Fig. 2 at *O*.)

These three auger tips are interchangeable; the impellers and half wings are not.

(2) *Dies.*—Tests were made with seven different brick dies, described as follows:

One zero degree taper nonlubricated brick die 8¾ by 4⅛ by 8 inches long.

Three 1° taper brick dies, each 8¾ by 4⅛ inches, in three lengths (6, 8, and 10 inches, respectively), all arranged for lubrication. (See figs. 4 and 5 at *D*.)

Two 2° taper brick dies, one 8¾ by 4⅛ by 8 inches long and one 9¾ by 4¼ by 9 inches long, arranged for lubrication.

One 4° taper brick die 8¾ by 4⅛ by 8 inches long, constructed of wood, lined with molybdenum, and arranged for lubrication.

(3) *Collective spacers.*—Four collective spacers the same diameter as the auger barrel were made of 12-inch-diameter standard W. I. flanged pipe, in lengths varying from 4 to 10 inches in increments of 2 inches. (Fig. 5 at *C*.) These spacers can be combined so as to make additional spacers varying in length from 12 to 24 inches in 2-inch increments. A tapered approach to the rectangular ingress of the die was provided by 45° fillets fitting inside of the spacer and held in position by a thin metal diaphragm.

(4) *Device used in studying the flow of plastic material through dies.*—A 12-inch-diameter collective spacer 11 inches long (fig. 6) is equipped with externally adjustable perforated needles extending into the center of the auger barrel at the tip of the auger. These needles are provided with flexible pipe connections, so that steam, water, or other liquids can be injected into the moving clay at any depth desired in order to determine their effect on column flow. They may also be used to inject colored liquids to stain the material as it leaves

the auger, so that the flow of the material through the spacer and die may be studied. The depth of the needles can be regulated from the outside by turning the depth plug *c*. (Fig. 6.) The pressure of the liquid to be injected is controlled by a pressure-reducing valve in the air line to the reservoir and by individual valves for each needle. (Fig. 6 at *B*.) The needles themselves assist in shredding the clay and breaking up auger laminations. Preliminary attempts to remove the entrapped air by applying a vacuum to these needles were not successful. The effect of an excess of air in the clay, however, was very marked. When compressed air at 50 pounds per square inch

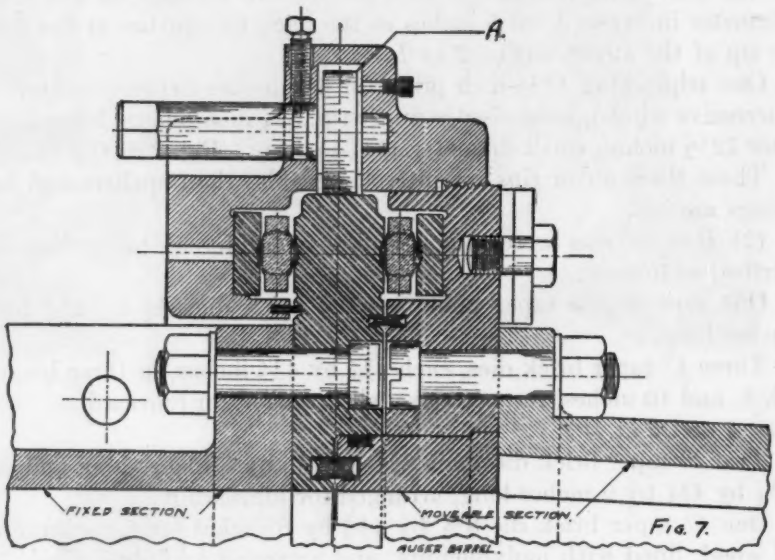

FIG. 7.—*Cross-section view of part of ball-bearing joint*

was forced into the material as it left the auger, large blisters were produced on the surface of the clay column.

(*c*) DYNAMOMETER ASSEMBLY.—(1) *Ball-bearing joint.*—The torsion-measuring apparatus shown in cross section of assembly (fig. 7) consists of two large hardened-steel disks or flanges (shown in fig. 8 at *A* and *B*). These disks are bolted to the flanges of the auger barrel and carry ball races to accommodate a series of $\frac{11}{16}$-inch-diameter hardened chrome nickel-steel balls. (Fig. 8 at *C*.) The outer edge of one of these disks (fig. 8 at *A*), called the "centering disk," is ground to provide a path for six hardened-steel rollers mounted on eccentric trunion pins (fig. 9; also fig. 7 at *A*). The other large-diameter disk (fig. 8 at *B*), called the "retaining flange," carries the die, the tapered nozzle or approach to the die, and a sealing sleeve that protects the ball-bearing joint (shown assembled in fig. 7). The circumference of the retaining flange is accurately machined to

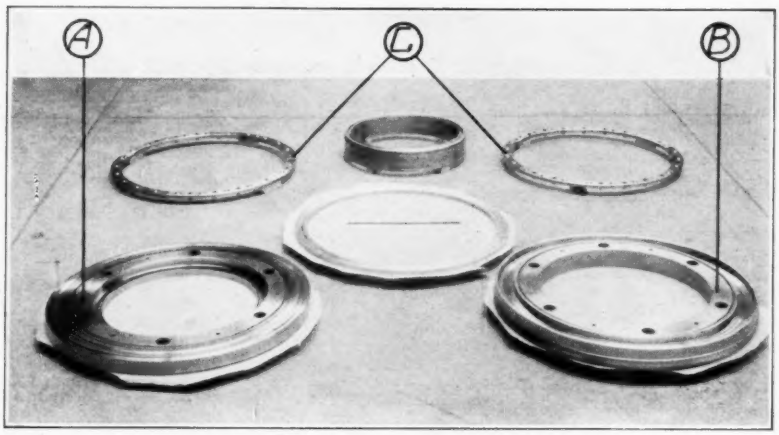

FIG. 8.—*Major parts of ball-bearing joint*

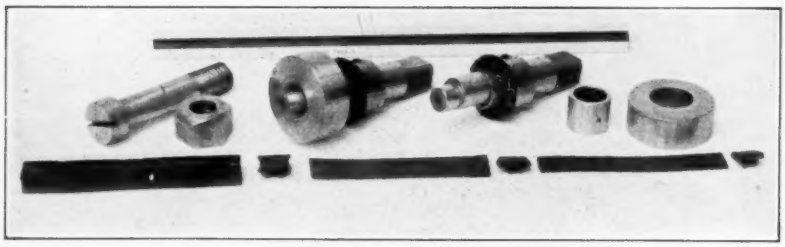

FIG. 9.—*Miscellaneous parts of ball-bearing joint*

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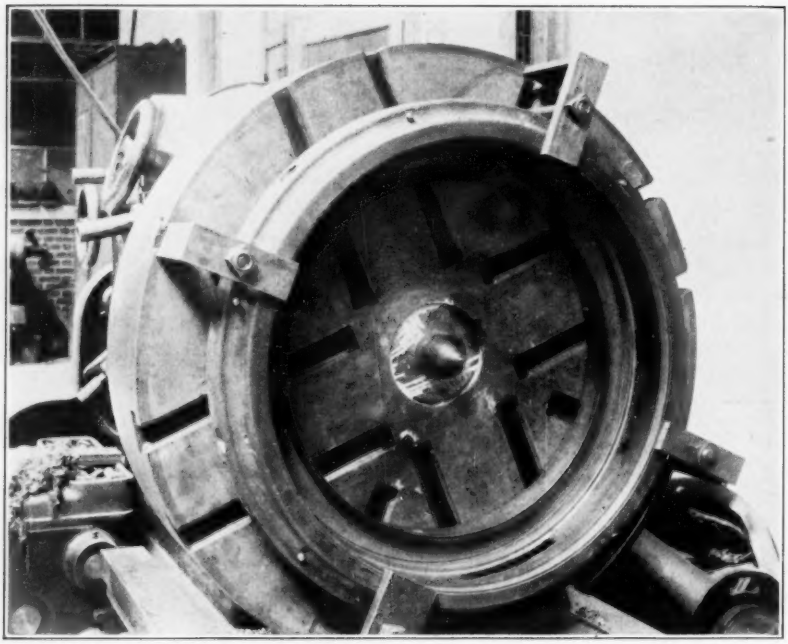

FIG. 10.—*Housing for ball-bearing joint (in process of machining)*

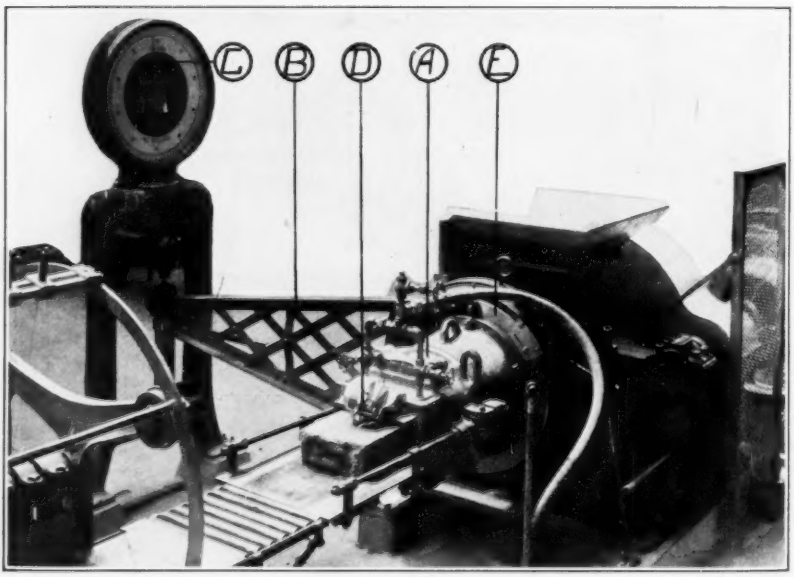

FIG. 11.—*Ball-bearing joint installation* (E)

provide a centering surface and a threaded portion which engages with an outer shell, shown in the process of manufacture, clamped to the faceplate of a lathe. (Fig. 10.) This cast-iron shell provides a housing for the ball-bearing joint, as well as providing adjustments for the annular rollers, and the two sets of ball bearings, all of which constitute a large inclosed dust-proof, water-tight drum having a storage space for lubrication, so that the rollers and ball bearings operate in a bath of oil (shown assembled in fig. 11 at *E*).

(2) *Dynamometer integrator.*—In the operation of the apparatus the useful work done by different designs of augers in forcing plastic materials through various combinations of spacers and dies is manifested in the form of a torsional moment of a constantly varying magnitude.

To determine the total amount of torque developed during a test, it is necessary to totalize these increments of torque. Consequently, an integrator which operates on the planimeter principle was installed on top of the dynamometer-scale drum. (Fig. 5 at *A*.) The registering mechanism of the integrator and the weighing mechanism of the scale are connected by a steelyard rod. (Fig. 5 at *G*.) A 5-inch-diameter revolving steel disk in the integrator is driven by a jointed shaft directly connected to the drive shaft of the auger machine. (Fig. 5 at *E*.) As the torsional moment varies in magnitude, a small hardened-steel friction wheel is moved across the face of the revolving disk a distance from the center proportional to the magnitude of the instantaneous torque. The friction wheel operates a revolution counter through a worm-and-gear reduction which registers the total integrated horsepower minutes developed by the auger.

(3) *Calibrating the scale and integrator.*—A 1,000-pound-capacity no-spring scale, modified by the installation of a new 1,500-pound-capacity scale head, was tested and calibrated to weigh within a possible error of 1 pound in 1,000 by suspending dead weights in increments of 50 pounds from the end of a cantilever beam. The error at 250, 500, 750, and 1,000 pounds was halved, as the load was repeatedly increased and decreased through the cycle from 0 to 1,000 pounds and back to zero.

The integrator is calibrated by—

(*a*) Adjusting the poise on the tare beam of the scale so that the dial hand registers zero with the auger machine running empty.

(*b*) The small planimeter wheel is brought to the center of the disk while the scale registers zero. This is done by adjusting the turnbuckle in the steelyard rod.

(*c*) With the auger machine running empty, dead weights in 250-pound increments are applied at the end of the dynamometer arm by means of an extension which can be attached at *F*. (Fig. 5.) The integrator, if in adjustment, will record 0 at no load, 8¾ h. p. m. at

250 pounds, 17½ h. p. m. at 500 pounds, 26¼ h. p. m. at 750 pounds, and 35 h. p. m. at 1,000 pounds, either during the calibration or an actual test, where the load is constantly changing.

The horsepower minutes (h. p. m.) consumed by the auger in extruding a certain weight of material is:

$$H.\,P.\,M.=\frac{PLN}{33{,}000}=\frac{PN}{1{,}000}$$

where P = the pull of the dynamometer arm on the scale in pounds.

L = the length of the dynamometer arm in feet $\times$ 2 π = 5.25 $\times$ 6.283.

N = the number of auger revolutions per minute.

When P is 1,000 pounds, the auger develops 1 horsepower minute per revolution.

3. OPERATION OF PLANT

(*a*) Measuring the Flow Pressure.—A piece of apparatus was also developed for determining the pressure required to force samples of the tempered materials through an orifice. This consists of a cylinder, 2¼ inches inside diameter and 8 inches long, closed at the top by a ½-inch hardened-steel plate and provided with a ½-inch-diameter orifice at the center. Through this orifice plastic material is expelled by a close-fitting piston 4 square inches in area, moving at the rate of three-fourths inch per minute. A small briquet left in the apparatus after the flow test is made is used for making a moisture determination.

The loaded cylinder is placed in a vertical position between the upper and lower plates of the 2,000-pound testing machine. This machine is sensitive to one-half pound and is accurate within ± 1 per cent up to 750 pounds.

(*b*) Making the Moisture Determinations.—Before tempering the screened clay its natural moisture is determined by drying three weighed samples to constant weight at 110° C. The moisture found in the material is expressed in per cent of the weight of the dry material and is the average of the three samples.

The moisture content of the tempered material is determined by taking the average of three moisture determinations made from samples of the plastic material taken just before each extrusion test.

(*c*) Column Speed and Capacity of the Extrusion Machine.—The column speed and capacity of the machine at 35 r. p. m. is approximately 8 feet per minute when using a die with a rectangular opening of 8¾ by 4⅛ inches. This is equivalent to about 10 tons of material, or 3,000 standard-size cut face brick per hour. A small lineal measuring device (fig. 11 at *D*) is attached to the egress of the die to measure the amount of material extruded in each test. From these data the total length and weight of the material extruded are obtained.

(*d*) MEASURING THE POWER ABSORBED BY THE AUGER.—By inserting the ball-bearing joint in the auger barrel as shown in Figure 11 at *E* and replacing the original plain thrust bearing at the rear end of the auger shaft by a tapered-roller thrust bearing (fig. 2 at *I*), it is possible to measure the actual power absorbed by the auger in forcing the material through the die, and incidentally establish a comparison between different designs of augers, collective spacers, and dies.

The ball-bearing joint previously described is made a part of the auger machine proper (fig. 2) and constitutes a swiveled auger barrel mounted on ball bearings and steel rollers in such a way as to carry the die, the approach to the die, the collective spacer, and the sleeve surrounding the auger. The swiveled auger barrel (fig. 11 at *E*) transmits the torque developed by the auger to the dynamometer scale by means of the 63-inch arm (fig. 11 at *B*). The magnitude of the torque developed is indicated by a hand which oscillates back and forth over a graduated dial. (Fig. 11 at *C*.) The total power absorbed by the auger on a measured quantity of material is recorded by an integrator attached to the weighing mechanism of the dynamometer scale, described under III 2 (*c*), (2).

(*e*) MAKING THE EXTRUSION TEST.—In operating the testing plant the clay or shale, which has been previously tempered to the proper consistency as determined by a preliminary flow test, is fed into the hopper of the auger machine by hand at a uniform rate.

After making necessary adjustments and changes to insure a smooth operation of the plant and the formation of a characteristic column of clay, which usually takes about two minutes, readings are taken simultaneously on all instruments, which include the electric-power meter and ammeter, the footage measurer, the integrator, and the timer. At the conclusion of the test the same instruments are again read. The difference between readings gives (1) current demand and total electric energy consumed, (2) useful power developed by the auger, and (3) weight of the material extruded during the test. The total work done by the auger in forcing the material through the machine is recorded by the integrator, and the length of the column of formed material is measured and recorded by the lineal counter. Defects of any kind appearing in the clay bar are noted. Immediately after completing the test the formed material is cut into small pieces and stored in the moisture-tight chamber (fig. 5 at *B*) preparatory to the next test.

The average flow pressure and average moisture content are determined from the three samples of the material taken just before each extrusion test. The instantaneous torsional reactions produced by the auger as it forces the material through the machine are noted from time to time during the test. From these data performance

curves are plotted, showing the weight of material extruded per h. p. m., the weight of material extruded per unit of time, the pressure per square inch required to produce flow, and the moisture content of the material at the time the test was made.[2]

IV. STUDIES OF CLAY AND SHALE IN THE DEVELOPMENT OF TEST PROCEDURE

1. PLASTICITY RANGE OF THE CLAYS AND SHALES STUDIED

It was considered that three clays or shales, such as are used in the industry, covering in a very general way the range from low through medium to high plasticity, would be sufficient to establish the data required for the design of the most important types of augers and dies.

2. PRELIMINARY STUDIES TO DEVELOP TEST PROCEDURE

Extrusion tests were made on a Virginia surface clay to ascertain the approximate maximum load demand for dynamometer-design purposes. (Table 1.) Also preliminary tests were made on a plastic shale from Illinois, a hard shale and a No. 2 plastic fire clay from western Maryland, and a medium plastic clay from eastern Maryland. These tests were made to ascertain the effects of slight changes in moisture content on the flow pressure and to develop methods of maintaining the moisture content of the tempered material within permissible limits.

TABLE 1.—*Preliminary test to ascertain the maximum efficient capacity of the auger machine used, and the corresponding value of current taken by the driving motor*

[Auger-machine equipment: Triple-wing auger, 8-inch—1° taper die, and 6-inch spacer]

VIRGINIA SURFACE CLAY—FUSION POINT 2,600° F.

Trial No.	Amperes at motor terminals	Average electric h. p. input	Remarks
1	49– 56.5	3.26	Motor operating chain drive only.
2[a]	90– 95	41.00	Motor operating auger machine full of clay.
3[b]	96–105	45.25	Clay churning back around impellers badly.
4	92–101	42.00	Do.
5	90– 98	39.00	Clay churning back around impellers reduced.
6	75– 90	34.50	Clay churning back around impellers eliminated.
7	62– 75	27.00	No churning at three-fourths capacity, die lubricated.
8	72– 85	33.00	No churning at seven-eighths capacity, die not lubricated.

[a] Circuit breaker tripped at 95 amperes.
[b] Circuit breaker adjusted to trip at 110 amperes.

NOTE.—The capacity of the auger machine at which the set-up operates the best corresponds to a measured value of current through the motor of between 75 and 85 amperes (obtained by taking the lowest limit of current in trial No. 6 and the highest limit in trial No. 8). Forcing the auger machine beyond this capacity results in the material churning back around the impellers. Also, when the current at the motor terminals exceeds 95 amperes, objectionable current and voltage fluctuations occur in the electric-power service.

[2] Four families of curves are plotted on each sheet; average values of moisture content, total flow pressure, pounds of material extruded per minute, and pounds of material extruded per horsepower minute (h. p. m.) comprise the ordinates. Four lengths of collective spacers comprise the abscissas.

3. PREPARATION OF THE CLAY

Proper preparation of the clay is important, inasmuch as improperly tempered clays are often responsible for badly formed clay columns. The effect on the working behavior of a clay by changing its water content during tempering is different in clays of different physical properties. Nevertheless, an increase in water content increases the ease of flow and the sticking properties, so that lamination planes when formed will knit more easily. On the other hand, the increase of water content may also decrease the viscosity and internal friction of the clay, so that differential flow of the center portion of the column is increased.

When the clay is put through the extrusion machine, it is affected the same as by an extra pugging, and, in general, the more a clay is pugged the more easily it is extruded. As an illustration, the medium plastic clay from eastern Maryland was tempered with 25.8 per cent water and pugged two and one-half minutes in a wet pan. This material, when put through the extrusion machine the first time, required 26.68 h. p. m. per ton of clay extruded, but when put through the second time required only 25.9 h. p. m. per ton of extruded material, a decrease in power of 2.9 per cent. To reduce this variable where the same material is to be used several times in making a series of tests, it is given an initial extrusion before an actual test is made.

4. EFFECT OF MOISTURE LOSS VERSUS REPEATED USE ON FLOW PRESSURE

Before reliable data could be obtained regarding the performance of various designs of augers and dies it was necessary to determine what changes take place in the flow pressure of the clays and shales due to changes in the moisture content and what changes take place due to repeated pugging and storage during a series of tests. Therefore, studies were made of the effects of variations in moisture as well as repeated extrusions on the flow pressure of a plastic shale from Danville, Ill., and a No. 2 plastic fire clay from Mount Savage, Md. The flow pressure of the plastic shale increased 11.3 per cent for a decrease of approximately 2.7 per cent of the total amount of water used in tempering the dry shale. The flow pressure of the No. 2 plastic fire clay increased 51.3 per cent for a decrease of approximately 2.3 per cent of the total amount of water used in tempering the dry clay. The decrease in moisture in both cases is due primarily to the material drying out during storage. The increase in flow pressure in each case is the result of the combined effect of moisture decrease and repeated pugging as the material passed through the auger machine. (See Tables 2 and 3.)

From the foregoing it is evident (1) that the flow pressure of the Illinois plastic shale is less affected by variations in moisture content,

repeated pugging, and storage than the No. 2 plastic fire clay; and (2) the enormous increase in flow pressure compared with the small decrease in water content in the region of the point of optimum plasticity illustrates the wide fluctuations in power required to operate an auger machine, due to variations in the water content of the tempered clay.

TABLE 2.—*Workable characteristics of a No. 2 fire clay from western Maryland*

[Auger-machine equipment used in all tests: Triple-wing auger, 11-inch spacer, two-cell hollow-tile die with cores removed]

Extrusion No.	Total moisture in the clay	Flow pressure	Clay extruded per h. p. m.	Remarks
	Per cent	*Lbs./in.²*	*Pounds*	
	26.70	62.0	----------	Moisture and flow at time clay was tempered, 24 hours before extrusion No. 1.
1	25.62	66.0	12.15	Moisture and flow before extrusion No. 1.
	25.60	78.5	----------	Moisture and flow after extrusion No. 1.
2	25.37	79.9	12.67	Moisture and flow before extrusion No. 2.
	25.38	85.5	----------	Moisture and flow after extrusion No. 2.
3	25.28	85.8	12.6	Moisture and flow before extrusion No. 3.
	25.27	90.8	----------	Moisture and flow after extrusion No. 3.
4	25.10	91.1	12.92	Moisture and flow before extrusion No. 4.
	25.04	99.9	----------	Moisture and flow after extrusion No. 4.

NOTE.—Clay stored under damp sacks 24 hours between extrusions.
Decrease in moisture from 25.62 to 25.04 is 2.27 per cent. The increase in flow pressure due to this moisture change is 51.3 per cent.

TABLE 3.—*Workable characteristics of a plastic shale from central Illinois*

[Auger-machine equipment used in all tests: Triple-wing auger, 11-inch spacer, two-cell hollow-tile die with cores removed]

Extrusion No.	Total moisture in the shale	Flow pressure	Shale extruded per h. p. m.	Remarks
	Per cent	*Lbs./in.²*	*Pounds*	
	23.05	64.9	----------	Moisture and flow at time shale was tempered, 24 hours before extrusion No. 1.
1	23.09	64.3	11.9	Moisture and flow before extrusion No. 1.
	23.30	54.6	----------	Moisture and flow after extrusion No. 1.
2	23.00	67.3	12.5	Moisture and flow before extrusion No. 2.
	22.84	61.5	----------	Moisture and flow after extrusion No. 2.
3 [1]	22.76	69.7	10.03	Moisture and flow before extrusion No. 3.
	22.80	72.0	----------	Moisture and flow after extrusion No. 3.
4	22.60	68.0	11.42	Moisture and flow before extrusion No. 4.
	22.47	71.5	----------	Moisture and flow after extrusion No. 4.

[1] Shale stored under wet sacks 48 hours between extrusions Nos. 2 and 3.

NOTE.—Shale stored under wet sacks 24 hours between extrusions except as noted.
Decrease in moisture from 23.09 to 22.47 is 2.68 per cent. The increase in flow pressure due to this moisture change is 11.3 per cent.

Tests similar to those referred to above were made on a brick shale from central Maryland and a brick clay from eastern Maryland with a view of obtaining a plastic material that would stand repeated pugging without materially affecting the properties governing its workable characteristics.

It was found that the flow pressure of the brick shale increased 184.0 per cent for a decrease of 8.6 per cent of the moisture content. (See Table 4.) The shale swedged poorly and could only be extruded twice; it would not flow under pressure when tempered with 14 per cent water, and with 18 per cent water it was very soft and would not hold its shape. With 16 per cent water it worked best but not satisfactorily, as some of the water squeezed out at pressures below 50 pounds per square inch. The flow pressure of the brick clay was found to remain practically constant during the first four extrusions, provided the variation in total moisture content was kept within about 5 per cent of the dry material by weight. When the number of extrusions were continued to six, the flow pressure changed 48 per cent for a moisture change of 9.27 per cent of the maximum moisture of the clay (see Table 5), which is small compared to the change in flow pressure of the No. 2 plastic fire clay (see Table 2).

These tests indicated that the eastern Maryland brick clay is a tough, medium plastic material, the flow pressure of which remains almost constant during repeated extrusions. (See Table 6.) Because of its practically constant working properties the eastern Maryland brick clay was used exclusively throughout the remainder of the tests herein reported. After tempering with 25½ per cent total water and pugging two and one-half minutes in a wet pan the clay could be used satisfactorily for 10 or 12 successive extrusion tests; however, the flow pressure gradually increased coincident with the decrease in moisture during each successive extrusion test.

TABLE 4.—*Workable characteristics of a hard, slaty brick shale from western Maryland*

[Auger-machine equipment used in all tests: Triple-wing auger, 11-inch spacer, two-cell hollow-tile die with cores removed]

Extrusion No.	Total moisture in the shale	Flow pressure	Shale extruded per h. p. m.	Remarks
	Per cent	*Lbs./in.*[1]	*Pounds*	
	16.91	98.0	----------	Moisture and flow at time shale was tempered, 24 hours before extrusion No. 1.
1	17.52	109.0	16.6	Moisture and flow before extrusion No. 1.
	16.86	124.0	----------	Moisture and flow after extrusion No. 1.
2	16.61	168.0	13.0	Moisture and flow before extrusion No. 2.
	16.52	187.6	----------	Moisture and flow after extrusion No. 2.
3	16.27	201.9	7.22	Moisture and flow before extrusion No. 3.
	16.02	309.5	----------	Moisture and flow after extrusion No. 3.
4	16.14	313.5	(1)	Moisture and flow before extrusion No. 4.
	15.35	350.0	----------	Moisture and flow after extrusion No. 4.

[1] Extrusion No. 4 could not be continued to completion on account of material becoming too dry to be extruded when operating the equipment at 50 per cent overload.

NOTE.—Shale stored under wet sacks 24 hours between extrusions.
Decrease in moisture from 17.52 to 16.02 is 8.61 per cent. The increase in flow pressure due to this moisture change is 184.0 per cent. Both of these values would be larger if the data for the uncompleted extrusion No. 4 were used.

TABLE 5.—*Workable characteristics of a medium-plastic brick clay from eastern Maryland*

[Auger-machine equipment used in all tests: Triple-wing auger, 11-inch spacer, two-cell hollow-tile die with cores removed]

Extrusion No.	Total moisture in the clay	Flow pressure	Clay extruded per h. p. m.	Remarks
	Per cent	*Lbs./in.*[2]	*Pounds*	
	24.67	67.2	----------	Moisture and flow at time clay was tempered, 24 hours before extrusion No. 1.
1	25.35	63.2	24.81	Moisture and flow before extrusion No. 1.
	25.20	60.7	----------	Moisture and flow after extrusion No. 1.
2	24.45	66.0	23.85	Moisture and flow before extrusion No. 2.
	24.40	64.0	----------	Moisture and flow after extrusion No. 2.
3	25.13	66.5	24.25	Moisture and flow before extrusion No. 3.
	25.10	73.2	----------	Moisture and flow after extrusion No. 3.
4	24.15	69.0	23.12	Moisture and flow before extrusion No. 4.
	24.10	69.2	----------	Moisture and flow after extrusion No. 4.
5[1]	23.76	72.0	20.82	Moisture and flow before extrusion No. 5.
	23.63	78.0	----------	Moisture and flow after extrusion No. 5.
6[2]	23.40	83.5	20.56	Moisture and flow before extrusion No. 6.
	23.00	93.5	----------	Moisture and flow after extrusion No. 6.

[1] Clay stored under wet sacks 72 hours between extrusions Nos. 4 and 5.
[2] Clay stored under wet sacks 48 hours between extrusions Nos. 5 and 6.

NOTE.—Clay stored under wet sacks 24 hours between extrusions except as noted.
Decrease in moisture from 25.35 to 24.10 is 4.91 per cent. The increase in flow pressure due to this moisture change is 9.5 per cent.
The decrease in moisture from 25.35 to 23.00 is 9.27 per cent. The increase in flow pressure due to this moisture change is 48 per cent.

TABLE 6.—*Workable characteristics of a medium-plastic brick clay from eastern Maryland; reground and retempered after being extruded six times* [1]

[Auger-machine equipment used in all tests: Triple-wing auger, 11-inch spacer, two-cell hollow-tile die with cores removed]

Extrusion No.	Total moisture in the clay	Flow pressure	Clay extruded per h. p. m.	Remarks
	Per cent	*Lbs./in.*[2]	*Pounds*	
	23.77	67.5	----------	Moisture and flow at time clay was tempered, 6 hours before extrusion No. 1.
1	23.77	67.5	20.58	Moisture and flow before extrusion No. 1.
	23.75	79.0	----------	Moisture and flow after extrusion No. 1.
2	23.90	63.0	20.03	Moisture and flow before extrusion No. 2.
	23.75	77.5	----------	Moisture and flow after extrusion No. 2.
3	23.75	76.0	20.07	Moisture and flow before extrusion No. 3.
	23.29	82.0	----------	Moisture and flow after extrusion No. 3.
4	23.10	81.0	20.29	Moisture and flow before extrusion No. 4.
	23.00	80.0	----------	Moisture and flow after extrusion No. 4.

[1] See Table 5.

NOTE.—Clay stored under wet sacks 24 hours between extrusions.
Decrease in moisture from 23.77 to 23.00 is 3.24 per cent. The increase in flow pressure due to this moisture change is 18.5 per cent.

A parallel series of 12 tests were made using "new material" with 25.4 per cent water in series (c) and "old or used retempered material" with 25.3 per cent water in series (b). The same combinations of equipment were used as in previous tests, consisting of a single-wing auger with a change of three 1° taper dry dies of 6, 8, and 10 inch lengths, respectively, and four different spacers with each change of die. These spacers were 4, 6, 8, and 10 inches in length. From the results of these 24 tests shown in Table 7 it is

evident that the gradual moisture drop is responsible for practically all the increase in the flow pressure. In general, the least change in the flow pressure is coincident with the least change in the moisture content. The total decrease in moisture content throughout the 12 tests was 2 per cent in the old and 1.8 per cent in the new. The corresponding increase in flow pressure required for the two materials due to drop in moisture amounted to 85 per cent for the old and 69 per cent for the new.

TABLE 7.—*Results of a parallel series of 12 tests on used and unused medium plastic Maryland brick clay*

Extrusion No.	Equipment combinations	Clay extruded per h. p. m.	Flow pressure on piston area 4 square inches	Total moisture in the clay	Values used in plotting moisture curves = $\frac{b+c}{2}$	Remarks
		Pounds	*Pounds*	*Per cent*		
2-b	1- 6- 4[1]	62.2	245	25.30	25.35	"b" denotes used (retempered) material.
2-c		77.2	222	25.40		"c" denotes new material.
3-b	1- 6- 6	61.0	275	25.07	25.13	
3-c		67.0	239	25.19		
4-b	1- 6- 8	54.0	282	24.96	25.07	
4-c		63.0	235	25.18		
5-b	1- 6-10	51.8	287	24.74	24.83	
5-c		54.0	250	24.93		46 hours after material was tempered.
6-b	1- 8-10	45.5	307	24.58	24.73	6-inch die replaced by 8-inch die.
6-c		46.8	258	24.89		
7-b	1- 8- 8	50.8	325	24.43	24.50	
7-c		55.0	270	24.57		
8-b	1- 8- 6	55.0	326	24.26	24.36	
8-c		65.4	295	24.46		
9-b	1- 8- 4	63.7	373	23.98	24.13	
9-c		70.2	302	24.29		95 hours after material was tempered.
10-b	1-10- 4	57.6	374	23.67	23.80	8-inch die replaced by 10-inch die.
10-c		58.0	317	23.94		
11-b	1-10- 6	55.8	394	23.59	23.72	
11-c		50.2	342	23.86		
12-b	1-10- 8	39.6	420	23.51	23.61	
12-c		40.0	350	23.72		
13-b	1-10-10	32.2	452	23.30	23.45	144 hours after material was tempered.
13-c		36.7	373	23.60		

[1] The first figure denotes the number of wings on the auger tip, the second the length of the die in inches, and the third the length of the collective spacer in inches.

The greatest variation in output per unit of power for any two corresponding extrusion tests of old and new material occurred when using a 6-inch die and a 4-inch spacer and amounted to 19¾ per cent, being less for the old material, when expressed in terms of the output of the new material. The least variation in output of old material, compared to that of the new material occurred when a 10-inch die and an 8-inch spacer were used, and amounted to 1¼ per cent of the output of the new material. (See Table 7, fig. 12.)

In the case of this particular clay the reuse of the tempered material has a comparatively small effect on its working properties from an extrusion-test standpoint so long as the moisture content is controlled within a variation of 1 or 2 pounds of water per 100 pounds of clay. (See Tables 5, 6, and 7.)

V. PRESENTATION OF DATA AND DISCUSSION OF RESULTS

1. CONDITIONS UNDER WHICH TESTS WERE MADE

The procedure in making these tests is essentially that outlined under III, 3, (*e*). The method of tempering the eastern Maryland clay used in these tests is described under IV, 3 and 4.

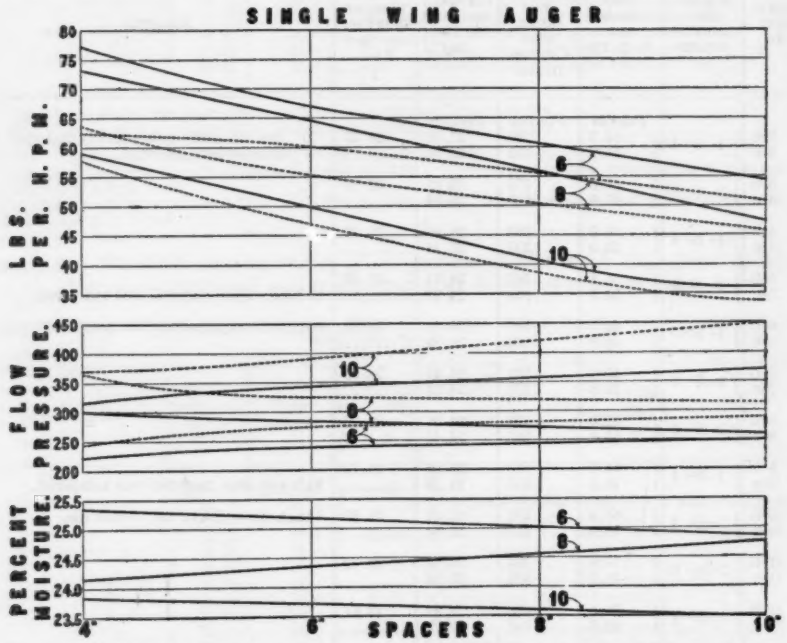

FIG. 12.—*Effects of moisture loss versus repeated use on flow pressure (workable characteristics)*

Solid-line graphs are for new (unused) material. Dotted-line graphs are for old (retempered) material

2. PERFORMANCE AND RELATIVE EFFICIENCY OF AUGERS

(*a*) SINGLE-WING AUGER.—The performance of a single-wing auger in extruding the clay is shown in Table 8 and Figure 13. The results are average values obtained experimentally in duplicate tests on each combination of equipment shown in the table.

TABLE 8.—*Average values of single-wing auger tests*

	Equipment combinations—Single-wing auger constant, taper 1° and egress 4½ by 8¾ inches for all dies											
	6-inch die constant, variable spacer length				8-inch die constant, variable spacer length				10-inch die constant, variable spacer length			
	1-6-4[1]	1-6-6	1-6-8	1-6-10	1-8-10	1-8-8	1-8-6	1-8-4	1-10-4	1-10-8	1-10-6	1-10-10
Pounds of clay extruded per h. p. m.[2]	80.4	68.6	61.5	54.0	46.8	53.2	65.8	71.2	66.2	54.8	36.7	34.6
Flow pressure in pounds per square inch	50.0	53.0	54.0	57.0	64.0	65.0	67.0	70.0	79.0	82.0	87.5	97.5
Per cent total moisture in the clay	25.9	25.6	25.5	25.3	25.2	24.9	24.8	24.7	24.3	24.2	23.9	23.4
Output in pounds of clay per minute	165	179	187	195	208	220	227	227	236	241	258	278

[1] The first figure denotes the number of wings on the auger, the second the length of the die in inches, and the third the length in inches of the collective spacer used in each test.
[2] H. p. m. denotes horsepower minutes.

It is apparent that the 4-inch-length spacer and 6-inch-length die combination gives the greatest output per unit of power, while the 10-inch-length die and 10-inch-length spacer combination gives the smallest output; however, the objectionable column defects coincident with the use of the 4-inch spacer—namely, cracking, tearing, and flaking—are almost entirely eliminated when a 6-inch-length spacer is used and are entirely overcome when an 8-inch-length spacer is used indicating that the most efficient single-wing auger equipment is narrowed down to an 8-inch-length spacer and a 6-inch-length die.

(*b*) DOUBLE-WING AUGER.—The performance of a double-wing auger, under comparable conditions of operation prevailing for single and triple wing augers regarding equipment and material, is shown graphically in Figure 14 and by Table 9 for average values resulting from a series of 40 tests.

TABLE 9.—*Average values of double-wing auger tests*

	Equipment combinations—Double-wing auger constant, taper 1° and egress 4½ by 8¾ inches for all dies											
	10-inch die constant, variable spacer length				8-inch die constant, variable spacer length				6-inch die constant, variable spacer length			
	2-10-10[1]	2-10-8	2-10-6	2-10-4	2-8-4	2-8-6	2-8-8	2-8-10	2-6-10	2-6-8	2-6-6	2-6-4
Pounds of clay extruded per h. p. m.[2]	26.8	22.80	25.00	40.20	42.70	39.40	34.10	31.70	34.40	37.50	41.60	44.20
Flow pressure in pounds per square inch	65.0	84.50	93.50	62.00	57.00	54.00	56.50	55.50	66.00	70.00	73.00	78.00
Per cent total moisture in the clay	24.7	23.84	23.52	24.74	25.28	25.23	24.96	24.85	24.56	24.53	24.32	24.10
Output in pounds of clay per minute	314	316	365	348	328	320	323	340	337	362	386	398

[1] In the various combinations the first figure denotes the number of wings on the auger, the second the length of the die in inches, and the third the length of the collective spacer in inches.
[2] H. p. m. denotes horsepower minutes.

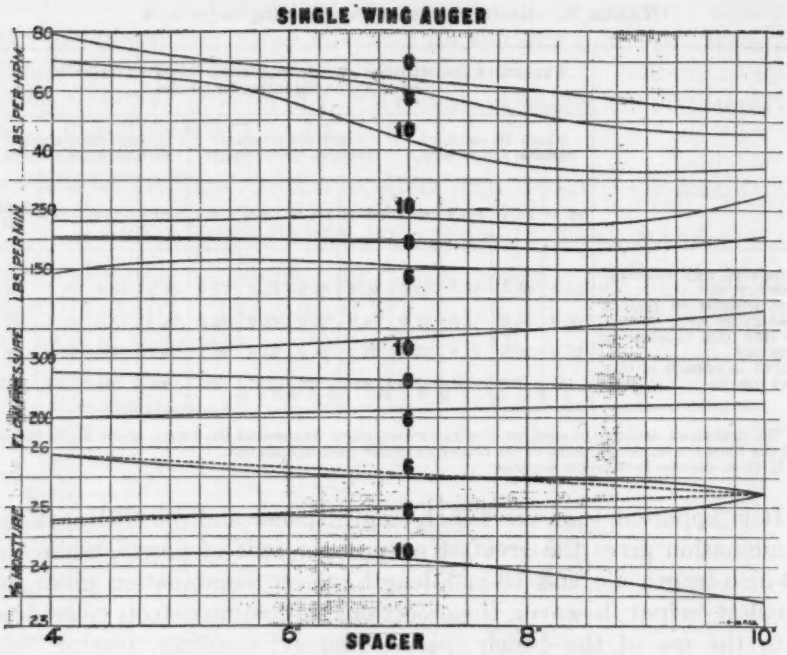

FIG. 13.—*Performance of a single-wing auger*

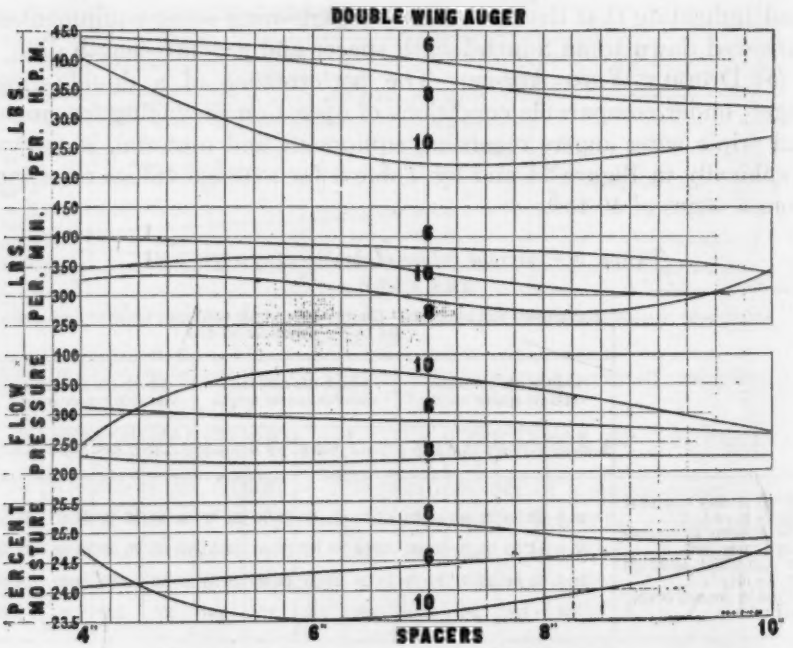

FIG. 14.—*Performance of a double-wing auger*

The 6-inch-length die and 6-inch-length collective spacer rate the highest output in pounds of clay per unit of power, without producing a defective column. The 4-inch-length collective spacer and 6-inch-length die have a slightly higher output per unit of power but produce transverse cracks and, therefore, a defective column.

(*c*) Triple-Wing-Auger.—The performance of a triple-wing auger under operating conditions comparable with those prevailing during tests on single and double wing augers is shown graphically in Figure

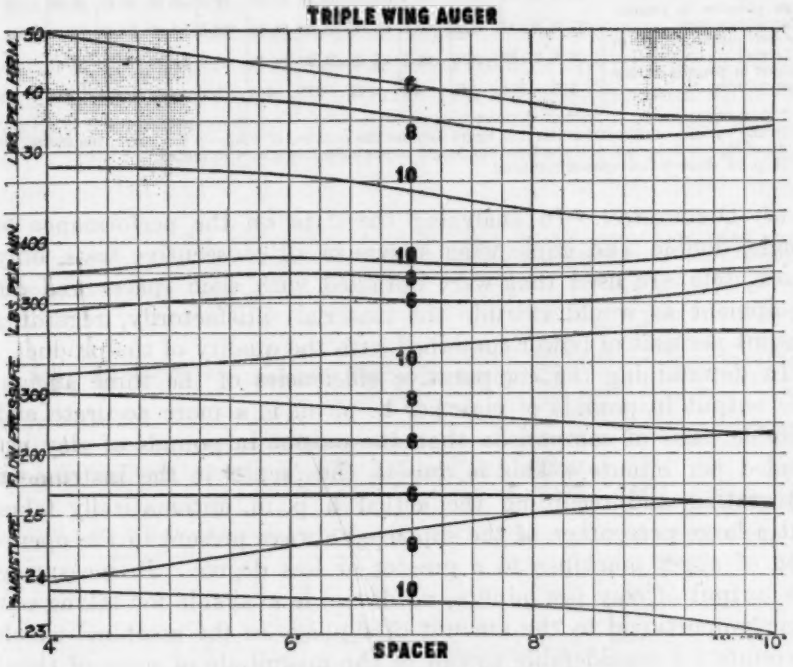

Fig. 15.—*Performance of a triple-wing auger*

15 and by Table 10 for average values resulting from a series of 30 tests.

As in the studies of single and double wing augers, the 4-inch-length collective spacer produced a defective column because of the proximity of the die to the auger. The results also show that collective spacers longer than 8 inches are wasteful of power.

As in the case of the single-wing auger, the most efficient combination of equipment based on output of clay per unit of power combined with quality of the clay column is an 8-inch-length spacer and a 6-inch-length die.

TABLE 10.—*Average values of triple-wing auger tests*

	Equipment combinations—Triple-wing auger constant, taper 1° and egress 4½ by 8¾ inches for all dies											
	6-inch die constant, variable spacer length				8-inch die constant, variable spacer length				10-inch die constant, variable spacer length			
	3-6-4[1]	3-6-6	3-6-8	3-6-10	3-8-10	3-8-8	3-8-6	3-8-4	3-10-4	3-10-6	3-10-8	3-10-10
Pounds of clay extruded per h. p. m.[2]	50.5	44.40	35.3	36.1	34.76	33.50	38.90	39.4	26.80	26.60	20.90	19.8
Flow pressure in pounds per square inch	53.0	56.00	57.5	60.0	60.00	65.00	71.50	76.0	83.00	91.00	99.00	101.0
Per cent total moisture in the clay	25.4	25.32	25.3	25.1	25.19	24.99	24.48	23.9	23.76	23.63	23.47	23.0
Output in pounds of clay per minute	312	349	343	363	363	377	456	327	352	376	348	397

[1] In the various combinations the first figure denotes the number of wings on the auger, the second the length of the die in inches, and the third the length of the collective spacer in inches.
[2] H. p. m. denotes horsepower minutes.

(*d*) DISCUSSION.—In analyzing the data on the performance of single, double, and triple wing augers in all consecutive tests, only those data are used that were obtained with such spacer and die equipment as would extrude the material satisfactorily, regarding output per unit of power combined with the quality of the product.

In determining the comparative efficiencies of the three augers, the output in pounds of clay per h. p. m. is a more accurate and reliable basis of comparison than the output in pounds of clay extruded per minute. This is due to the fact that the instrument integrating and recording the actual h. p. m. automatically takes out a large percentage of the slippage,[3] always present in the operation of auger machines to a greater or less degree. In measuring the output of clay per minute, no device is available for taking out time proportional to the amount of slippage in the machine, which accounts for considerable spread in the magnitude of some of these values. However, corrections have been made by extrapolation where slippage is known to exist, for the sake of studying the actual trend of the results.

From the foregoing it appears that the greatest output per minute occurs where the flow pressure is greatest, also the slippage is the least where the moisture content is the least, indicating that a slight excess of water above that required to produce optimum plasticity decreases viscosity of the clay, and consequently increases slippage.

The average relative efficiencies of the single, double, and triple wing augers based on the output per unit of power (see Table 11, column 7) are in the order and magnitude of 100, 60.57, and 60.53,

[3] Slippage is a term used here to designate a condition existing in auger-extrusion machines where the speed of travel of the extruded material slows down or stops entirely and is usually due either to irregularity in the quantity of material carried forward by the impeller blades or to very wet or very dry material becoming wedged in the auger spirals and revolving with the auger.

respectively. The average relative efficiencies of the same three augers based on the output of material per unit of time (Table 11, column 8) are in the order and magnitude of 49.3, 90.1, and 95.1, respectively, which is the reverse of the order of magnitude of efficiencies of the same three augers based on the output per unit of power. These data indicate that the pressure in the extruded material is increased more by augers having multiple wings than by augers having a single wing and that the friction loss due to the material sliding through the auger wings increased as the number of wings on the auger increased.

It is obvious that the most important design factors are primarily those having to do with the development of an auger capable of delivering the greatest volume of material with the greatest axial thrust per unit of power consumed. Of the three types of augers used in these tests, the single-wing auger is the most efficient in point of power consumption and is the type the most capable of such development.

TABLE 11.—*Average relative efficiencies of single, double, and triple wing augers when operating in combinations using 6 and 8 inch dies and 6 and 8 inch spacers*

Equipment combinations	Flow pressure	Moisture in the clay	Output in pounds per h. p. m.[2]	Output in pounds per minute, measured	Output in pounds per minute, corrected for slippage	Efficient in pounds per h. p. m.	Efficient in pounds per minute
6-INCH-LENGTH 1° TAPER DRY DIE AND A 6-INCH-LENGTH COLLECTIVE SPACER							
	Lbs./in.²	*Per cent*				*Per cent*	*Per cent*
1-6-6[1]	53.0	25.57	68.60	167.5	179	100.0	46.4
2-6-6	73.0	24.32	41.60	386.0	386	60.7	100.0
3-6-6	56.6	25.32	44.40	312.0	349	64.8	90.5
6-INCH-LENGTH 1° TAPER DRY DIE AND AN 8-INCH-LENGTH COLLECTIVE SPACER							
1-6-8	54.0	25.50	61.50	155.3	187	100.0	51.7
2-6-8	70.0	24.53	37.50	362.0	362	61.0	100.0
3-6-8	57.5	25.31	35.37	300.0	343	57.6	95.0
8-INCH-LENGTH 1° TAPER DRY DIE AND A 6-INCH-LENGTH COLLECTIVE SPACER							
1-8-6	67.0	24.88	65.83	201.2	227	100.0	49.8
2-8-6	54.0	25.23	39.40	320.0	320	60.0	70.2
3-8-6	71.5	24.48	38.90	440.0	456	59.2	100.0

[1] In the various combinations the first figure denotes the number of wings on the auger, the second the length of the die in inches, and the third the length of the collective spacer in inches.
[2] H. p. m. denotes horsepower minutes.

It is apparent from the performance curves (figs. 13, 14, and 15) that the output per unit of power for all designs of augers and all designs of brick dies and spacers decreases as the length of the die or the length of the collective spacer increases.

3. COLLECTIVE SPACERS

(*a*) EFFECT OF LENGTH ON POWER CONSUMPTION AND QUALITY OF THE PRODUCT.—The length of the intermediate collective chamber or spacer between the tip of the auger and the ingress of the die is a very important factor in the quality of the clay column and

in the power consumption. In auger machines equipped with brick dies the greater the length of the collective spacer the greater the power consumption per thousand brick extruded.

Four-inch-length collective spacers produce transverse column cracks as the result of a variable and uneven pressure behind the die

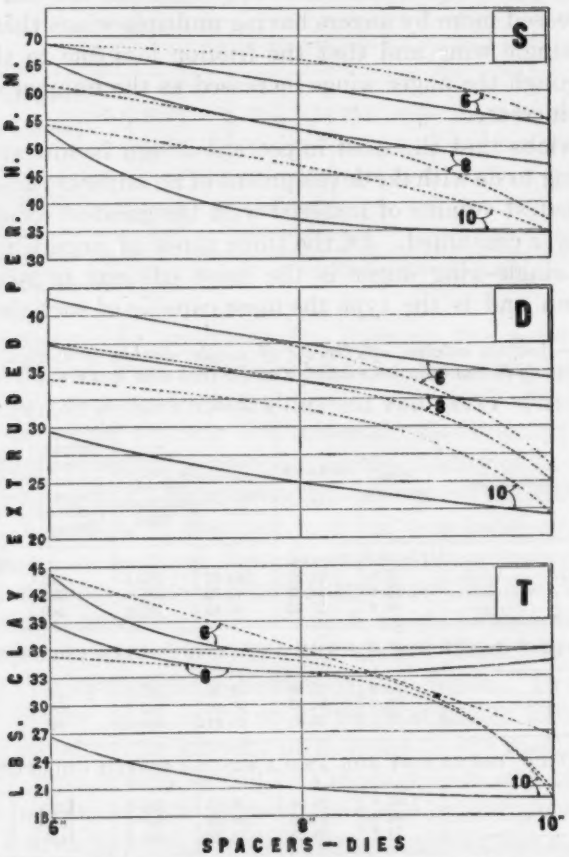

FIG. 16.—*Comparative effects of die and spacer lengths on output*

NOTE.—Pounds of clay extruded per horsepower minute plotted on the ordinate, with dies and spacers varying in length plotted on the abscissa, for different augers as indicated.
S, single-wing auger.
D, double-wing auger.
T, triple-wing auger.
Dotted lines denote spacer constant with 6, 8, and 10 inch dies.
Solid lines denote dies constant with 6, 8, and 10 inch spacers.
Different spacers and dies are plotted on the abscissa in the same units, viz, 6, 8, and 10 inch for the three different charts, S, D, and T. (See Table 12.)

ingress, resulting in a zigzag motion of the clay column as it emerges from the die. This is because the die is so close to the tip of the auger that the individual thrusts from the wings on the auger as these wings pass the horizontal plane of the die are transmitted through the die to the extruded clay column.

In all tests where spacers 4 inches or less in length were used with single, double, and triple wing augers, transverse column cracks were produced. While 6-inch spacers gave satisfactory results with double and triple wing augers, it was evident that 8-inch spacers are preferable where single-wing augers are used, since the greater volume of elastic material under pressure in the 8-inch spacer more completely dissipates the excessive alternate thrusts characteristic of the single-wing auger. The 8-inch spacer also has the effect of producing better equalization of pressure across the ingress opening of the die.

(*b*) DISCUSSION.—Collective spacers more than 8 inches in length are of no special advantage in molding common brick columns. In special cases, however, where a very straight flowing clay column of extra good structure is desired, it may be advantageous to use collective spacers longer than 8 inches. Nevertheless, any length of collective spacer greater than that required to overcome uneven flow through the die due to the thrust of the auger wings is unnecessary and wasteful of power.

The effect of collective spacer length on output per unit of power and quality of the ware does not follow the same law that applies to the effect of the length of the brick die on output per unit of power and quality of the ware.

By referring to Table 12 and Figure 16 the relative effect on output per unit of power caused by increasing the length of the die in increments of 2 inches from 6 to 10 inches is shown by the length of the intercepted ordinates between the solid curves as they cross the page from left to right.

TABLE 12.—*Average values (used in plotting graphs, fig. 16), showing the comparative effect of die length and spacer length on output per h. p. m.*

SINGLE-WING AUGER

Dies constant; spacers varying				Spacers constant; dies varying			
Length of dies			Length of spacer	Length of die	Length of spacers		
6 inches	8 inches	10 inches			6 inches	8 inches	10 inches
Clay extruded per h. p. m.					Clay extruded per h. p. m.		
Pounds	*Pounds*	*Pounds*	*Inches*	*Inches*	*Pounds*	*Pounds*	*Pounds*
68.60	65.83	53.20	6	6	68.60	61.50	54.00
61.50	53.20	37.00	8	8	65.83	53.20	46.80
54.00	46.80	34.60	10	10	54.80	36.75	34.60

DOUBLE-WING AUGER

41.60	37.40	29.70	6	6	41.60	37.50	34.40
37.50	34.10	25.10	8	8	37.30	34.10	31.70
34.40	31.70	21.90	10	10	26.50	25.00	21.90

TRIPLE-WING AUGER

44.40	38.90	26.60	6	6	44.40	35.37	36.10
35.37	33.50	20.90	8	8	36.00	33.50	34.76
36.10	34.76	19.80	10	10	26.60	20.90	19.80

NOTE.—A medium plastic clay from eastern Maryland used in all tests. The total moisture content varied from 25.57 per cent maximum to 23 per cent minimum.

The corresponding effect on output per unit of power caused by increasing the length of the spacer by 2-inch increments from 6 to 10 inches is likewise shown as the dotted curves cross the page from left to right.

By comparing the slope of each solid curve with the slope of each corresponding dotted curve as they cross the 6, 8, and 10 inch ordinates of the graph, it is seen that an increase in the length of the die causes nearly twice the decrease in output per unit of power as does a corresponding increase in the length of the spacer.

Although insufficient data have been obtained from which definite conclusions can be drawn, those which have been obtained indicate that any length of die greater than that necessary to form a clay column of satisfactory structure is unnecessary and rapidly decreases the output efficiency of the machine. A corresponding increase in the length of the spacer, however, is apparently independent of the dimensions of the clay column molded and, as compared with the effect of increasing the length of the brick die, only slightly reduces the output efficiency of the machine.

4. BRICK DIES

(*a*) Effect of Length on Power Consumption and Quality of the Product.—(See 3 (*a*), Collective spacers.)

(*b*) Effect of Lubrication of Die on Power Consumption and Quality of the Product.—Although the study of the lubrication of dies is to be undertaken in a future investigation, preliminary tests have been made which furnish interesting tentative information subject to verification by more complete experimental data.

The theory of lubrication of brick and hollow-tile dies is similar to that of oil lubrication of the moving metal surfaces in contact with each other in machinery. In the case of plastic materials we are not limited to oils, but can use water, steam, or even air. In lubricating dies for molding plastic materials it is necessary to provide a constant film or cushion of lubricant between the plastic material and the metal, so that the two materials do not come in contact. To accomplish this it is necessary to force the lubricant into the die at pressures sufficient to offset the internal pressure of the plastic material against the metal surfaces of the die.

Serious difficulties are encountered in attempting to equalize this varying pressure of the material against the inner walls of the die when using oil, water, steam, or other liquids as a lubricant, it being necessary to constantly regulate the pressure of the lubricant in order to balance the variable internal pressure of the material and maintain the film or cushion between the plastic material and the die; otherwise the lubricant will spurt out in streams, cutting grooves in the column and producing a "slimy," defective surface.

With air as a lubricant the pressure does not require close regulation. Much smaller supply pipes and orifice openings can be used to supply the required volume and pressure. The finish of the molded column is not impaired by air lubrication. The use of air as a lubricant for brick dies is shown, by experimental data, to decrease the power consumption from 8 to 10 per cent, depending to some extent on the physical characteristics of the materials extruded.

The only cost of compressed air as a lubricant is the equipment and power required for its application. Oils and such liquids for lubrication are not available without more or less expense and trouble. Where steam is used to lubricate the die in plants electrically operated, special provisions must be made for producing and maintaining the steam by operating a boiler at the required pressure. The equipment for air lubrication consists of a small power-driven compressor and necessary piping to supply air to the die. Usual temperature changes do not affect the flow; it is safe, easily applied, and free from detrimental effects on the product.

Each lubrication test was made in two steps. In the first step the die was operated dry prior to lubrication. In the second step the die was lubricated either by steam, water, or air. The effects of steam, water, and air lubrication on 1°, 2°, and 3° taper, 8-inch length standard-size cut brick dies of the four-liner Niedergesaess type are shown in Table 13, and graphically in Figure 17.

The results of lubrication on the 3° taper die show that steam lubrication increased the dry-die output per unit of power 25 per cent. Water increased it 20.6 per cent, and compressed air increased it 8.3 per cent indicating that steam as a lubricant is three times as effective as compressed air and one-fifth more effective than cold water, all other conditions being considered constant.

TABLE 13.—*Effect of air, steam, and water lubrication on the performance of 1°, 2°, and 3° taper brick dies*

	Equipment combinations—Single-wing auger and 6-inch collective spacer constant											
	8-inch length, 1° taper die constant, variable conditions of lubrication				8-inch length, 2° taper die constant, variable conditions of lubrication				8-inch length, 3° taper die constant, variable conditions of lubrication			
	Dry die	Air at 8 pounds per square inch	Steam at 10 pounds per square inch	Water at 8 pounds per square inch	Dry die	Air at 10 pounds per square inch	Steam at 15 pounds per square inch	Water at 12 pounds per square inch	Dry die	Air at 25 pounds per square inch	Steam at 30 pounds per square inch	Water at 25 pounds per square inch
Pounds of clay extruded per h. p. m.	88.00	93.00			86.00	90.00			74.00	80.10		
	91.00		113.10		86.60		105.50		78.80		98.40	
	80.00			100.00	77.70			92.80	68.00			82.00
Flow pressure in pounds per square inch	67.00	67.00			70.00	70.00			73.00	73.00		
	68.50		68.50		72.00		72.00		81.00		81.00	
	73.00			73.00	76.00			76.00	85.00			85.00
Per cent total moisture in the clay	24.73	24.73			24.60	24.60			24.12	24.12		
	24.72		24.72		24.38		24.38		23.86		23.86	
	24.43			24.43	24.21			24.21	23.84			23.84
Output in pounds of clay per minute	323.00	268.00			346.00	309.00			385.00	321.00		
	313.00		308.00		331.00		325.00		333.00		328.00	
	328.00			315.00	342.00			327.00	391.00			368.00

The comparative efficiencies of steam, water, and air as lubricants are questionable because of insufficient data. The dies were obtained on the open market and were designed especially for steam lubrication, and therefore may not be suitable for the most efficient application of water or air. Nevertheless, the results are valuable, indicating that air has certain advantages and possiblities as a lubricant sufficient in value to warrant further investigation.

(*c*) Discussion.—Long dies produce greater retardation of flow at the corners, due to increased friction, while short dies do not overcome the zigzagging motion to the clay column, thus producing

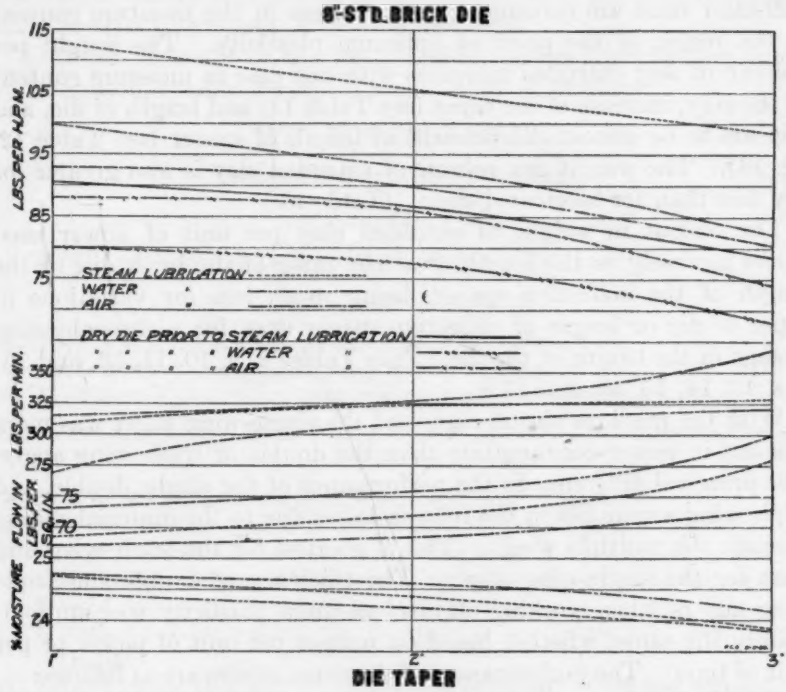

Fig. 17.—*Effects of air, steam, and water lubrication on 1°, 2°, and 3° taper dies*

column cracks, especially where the die is set within 6 inches or less of the auger tip. Excessive taper causes increased friction and differential flow. Greater auger thrust is required to overcome the resulting increased friction, and the differential flow tends to destroy the helical structure.

The outlet dimensions of a high-tapered die must be smaller than those of a low-tapered die to produce the same-sized clay column, due to greater elastic compression in the die and the resultant expansion of the clay as the column emerges from the die (33). Any die taper greater than that required for maximum discharge and to eliminate

excessive auger laminations is wasteful of power and produces a poor structure, because the expansion of the clay column is accompanied by a weakening of the clay bar. More complete experimental data, however, are necessary before the principles governing the proper relation of the taper of a die to its length can be definitely determined.

VI. CONCLUSIONS

Results of the foregoing studies are summarized in the following conclusions:

Marked changes in the flow pressure for plastic clay or shale in the stiff-mud state are coincident with changes in the moisture content in the region of the point of optimum plasticity. The weight per volume of clay extruded increases with decrease in moisture content of the clay, increase of die taper (see Table 13) and length of die, and appears to be almost independent of length of spacer (see Table 12, fig. 16). The weight per volume of extruded clay is also greater for dry dies than for lubricated dies. (Table 13.)

The output in weight of extruded clay per unit of power used varies inversely as the length or as the taper of the brick die, or the length of the collective spacer, being much less for variations in taper of die or length of collective spacer than for a corresponding change in the length of the die. (See Tables 8, 9, 10, 11, 12, and 13; figs. 13, 14, 15, 16, and 17.)

With the medium plastic clay used the single-wing auger was more efficient in power consumption than the double or triple wing auger. The principal difference in the performance of the single, double, and triple wing augers lies in the friction losses due to the material sliding through the multiple wings. This is greatest for the triple-wing and least for the single-wing auger. The efficiency of double and triple wing augers when working clays of medium plasticity was approximately the same, whether based on output per unit of power or per unit of time. The performances of the three augers are as follows:

The single-wing auger extrudes a greater weight of clay per unit of power than the double or triple wing auger, but must be farther from the die to overcome uneven flow.

The double-wing auger reduces uneven flow by giving a more even pressure to the clay column than the single-wing auger.

The triple-wing auger gives a more even pressure through the die than either the single or double wing auger, but occupies slightly more space in the auger barrel, develops more friction, and is not as efficient for short, lean clays as a single or double wing auger.

For producing a clay column free from objectionable defects, the combination giving the maximum quantity of material extruded per unit of power was a single-wing auger, with an 8-inch spacer and a 6-inch die, whereas the maximum quantity of material extruded per

minute was obtained with a triple-wing auger, an 8-inch spacer, and a 6-inch die.

The following observations as to the probable advantages and possibilities of the apparatus developed and used for this work seem justified:

1. It will measure small differences in the torque required to extrude clay and shale of different plastic consistencies under varied conditions of operation as regards auger, spacer, and die equipment.

2. It affords a practical means of studying the workable characteristics of clays and shales and provides a reliable method of determining the auger and die equipment best suited to their physical properties and the class of product to be manufactured.

3. It can be used to study the effects of various lubricants on power consumption, quantity output, and quality of product.

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RP30. Equipment for routine spectral transmission and reflection measurements. H. J. McNicholas.

RP31. Effect of temperature change on the color of red and yellow Lovibond glasses. Deane B. Judd.

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